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Contents

The Influence of Boron on the Growth of the Soybean Plant. Gilbeart H. Collings.......... 83

Organic Matter Changes in Two Soil Zones, as Influenced by Difference in Form, Fineness, and Amount of Calcic and Magnesic Materials. W. H. MacIntire, W. M. Shaw and Esther M. Crawford.......... 107

The Phenomena of Contraction and Expansion of Soils When Wetted with Water. George John Bouyoucos.......... 119

Colloidal Behavior of Soils and Soil Fertility: III. Cation Replacement and Saturation of Soil with Ca. J. S. Joffe and H. C. McLean.......... 127

A Study of the Factors Influencing the Efficiency of Different Forms of Nitrogen as Related to Soil Type and Cropping System in the Atlantic Coastal Plain Region: Part I. Arthur Matthias Smith.......... 137

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THE INFLUENCE OF BORON ON THE GROWTH OF THE SOYBEAN PLANT[1]

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INTRODUCTION

Widespread interest was shown a few years ago in the influence on plant growth of fertilizers carrying boron. Because of that interest, this investigation was made to study carefully the influences of boron on the growth of the soybean plant with particular attention to the detection of all toxic and stimulating actions of the element.

As early as 1857 Wittstein and Apoiger (26) reported the presence of boron in the seed of Abyssinian Saoria (*Maessa picta*). Callison (9), in 1890, found the element to be present in fifty-one miscellaneous plants. From time to time other investigators have reported its presence in various plants and plant parts, so that at the present time its distribution in the plant kingdom is known to be almost universal.

The experiment stations of this country conducted many field tests during, and immediately after, the World War to determine to what extent borax might be toxic to such field crops as cotton, corn, and potatoes. This work was necessary because of the widespread damage to field crops by certain American potash fertilizers that contained borax. Toxicity to plants was amply demonstrated when boron in the form of borax was applied in comparatively large quantities. In certain cases, such as in the results secured by Neller and Morse (19), small quantities of boron appeared to stimulate plant growth. In most of this work, however, especially in those cases where the experiments were carried on under field conditions, no minute study of the physiological influences of boron on plant growth has been attempted.

The function of boron in the plant, if it has any, is problematical. Warington (25) of the Rothamstead Experiment Station believes that the action of boron is "probably nutritive rather than catalytic;" thus she accepts its presence as an essential element for at least the broad bean plant.

Experimental procedure and general methods

The influence of boron on the growth of soybeans, and its relative influence when applied in the form of boric acid, potassium borate, and sodium borate, or borax, was studied

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under five heads: first, on germination; second, on the seedling phase of growth of soybeans in nutrient solutions; third, on plants grown to maturity in nutrient solutions; fourth, on plants grown in sand; and fifth, on plants grown in soil.

The Manchu variety of soybeans (*Soja max*) was used throughout the experiments. In order to secure the greatest uniformity among the plants grown, a pure line strain of the variety was used. The seed were hand graded and were planted in moist sphagnum moss. In about one week after planting, selected seedlings were transplanted to the culture jars or pots, which contained the solutions, sand, or soil.

An excellent grade of seashore fine sand, secured from a pit, was used in all the sand cultures. The same sand was used in all the germination experiments, but it was first thoroughly washed free of all clay particles.

The soil used in the soil cultures was Norfolk coarse sand secured in the vicinity of Milltown, New Jersey. The soil used in the germination experiments was Sassafras loam, secured on the farm of the New Jersey Agricultural Experiment Station.

For most of the pot culture work, glazed earthenware pots of a capacity of about two kilos of dry sand were used. Into each pot was weighed 1700 gm. of dried sand or soil. All pots were tared with coarse washed gravel.

To each pot of the sand and soil cultures, a complete fertilizer, consisting of 0.187 gm. of chemically pure ammonium sulfate, 0.75 gm. of acid phosphate, and 0.25 gm. of chemically pure potassium chloride, was applied. The acid phosphate was thoroughly mixed with the dry sand or soil, but the potassium chloride was first dissolved in water and one-half added just before the seedlings were transplanted, and one-half about three weeks later. The ammonium sulfate was also dissolved in water and applied in three weekly installments. The first applications of ammonium sulfate and of potash were made at the same time.

The culture jars used in the water culture work were of colorless glass, and had a capacity of 900 cc. (1 quart) and 1800 cc. (2 quarts). These jars had for some years been used for culture work, and were, therefore, thoroughly seasoned.

Three seedlings were transplanted to each jar or pot. For the water culture jars, the three seedlings were mounted in a double-piece paraffined cork stopper, such as that devised by Tottingham (23) and placed in each culture jar. Cylindrical shells of manila paper were placed around the jar to exclude the light from the plant roots. These paper shells were also used around all reservoirs of solutions to prevent the growth of algae, and to prevent such chemical action of light as the conversion of nitrates to nitrites as has been reported by Baudish (4).

After the application of the boron to the sand and soil cultures, the moisture was maintained at 12.5 per cent of the dry weight of the sand or soil by weighing once each day and replacing the loss of weight with distilled water. Similarly, all germination tests conducted in sand were maintained at 12.5 per cent water by weighing once each day. Two weighings were sometimes made on hot days when excessive evaporation was taking place.

A modification of Tottingham's four-salt solution $T_1 R_1 C_3$, as devised by Jones and Shive (15) was used in all of the water culture work. This solution is made up of $(NH_4)_2SO_4$, KH_2PO_4, $Ca(NO_3)_2$, and $MgSO_4$ in volume molecular proportions of 0.0014, 0.00211, 0.00146, and 0.01659 respectively. The stock solutions of these chemicals were made up to one-half molecular concentrations.

Iron was added to the water cultures in the form of soluble ferric phosphate in amounts equivalent to about 0.25 mgm. per liter of the nutrient solution. The ferric phosphate was made up in concentrations equivalent to about 1 mgm. of iron per cubic centimeter of solution. This stock solution was always prepared just before being added to the culture solutions. This element was added to the culture solutions when the plants appeared to need it.

In order to incorporate different amounts of boron in each culture solution, it was found necessary to make up each culture separately, although the same nutrient solution was used in all the water culture work.

All cultures of all series of plants grown during the seedling phase were constantly re-

newed according to a drip and drain method somewhat similar to that devised by Allison and Shive (2). One quart of solution was allowed to pass through the system every twenty-four hours. From time to time the glass siphons, which were exposed to light, were washed in acid and then in distilled water to free them from algae.

In most cases, duplicate series were grown at the same time. In such cases the corresponding cultures of each series were placed adjacent to each other, in order that environmental conditions might be as nearly alike as possible. Weekly records were kept of all changes taking place in the uniformity of the tops of each series, and of the roots of all plants grown in water cultures. When the growth period of each series was completed, the tops were severed from the roots and a determination of the green weight of both tops and roots

TABLE 1

Influence of boric acid, potassium borate, and borax on germination

BORON PER LITER OF SOIL SOLUTION	PERCENTAGE OF GERMINATION AT INTERVALS AFTER SEEDLINGS APPEARED*											
	Sand media									Soil (sassafras loam) media		
	Boric acid			Potassium borate			Borax			Borax		
	Second day	Fourth day	Sixth day	Second day	Fourth day	Sixth day	Second day	Fourth day	Sixth day	Second day	Fourth day	Sixth day
mgm.												
0	80	85	87	75	85	90	65	70	70	75	77	80
0.5	92	97	97	72	77	77	80	80	80	90	92	92
1.0	85	90	90	82	90	90	62	80	80	82	85	85
10.0	82	97	100	70	75	82	57	67	67	77	82	85
25.0	52	75	82	70	75	77	30	45	45	72	82	82
50.0	50	70	72	45	77	77	22	32	32	70	70	72
100.0	22	30	40	5	32	45	5	10	10	80	80	80
150.0†	22	32	35	15	15	17	10	12	20			
200.0†	12	15	20	7	15	15	0	5	5			
250.0	0	0	0	0	0	0	0	0	0	87	95	95
500.0	0	0	0	0	0	0	0	0	0	52	55	57
1000.0	0	0	0	0	0	0	0	0	0	30	40	40

* Average of two tests.

† These two concentrations were used in another experiment at a later date.

was made at once. The roots were first gently rinsed with distilled water and then placed on blotting paper for a few minutes before weighing. Both the roots and tops were placed in manila bags and allowed to dry at ordinary temperature in the greenhouse. They were then placed in an oven and kept at 100° C. for 24 hours. The contents of each bag were then weighed and the dry weight of each culture was determined.

THE INFLUENCE OF BORON ON GERMINATION

The germination experiments were made in No. 2 enamel pans. Into each pan, 200 gm. of dry washed sand, or in one experiment, of dry Sassafras loam soil, was weighed and leveled. Twenty hand-selected seed were uniformly distributed over the surface and an additional 800 gm. of dry washed sand or of the dry soil was added. Into each pan was then poured 125 cc. of a solution containing the desired amount of boron.

Records were taken for six successive days after the first seedlings appeared above the surface of the sand or soil. The number and appearance of the seedlings were recorded each day. All germination experiments were run in duplicate.

Experiments conducted in washed sand

The results of all experiments conducted in washed sand are given in table 1. It will be observed from these data that 250 mgm. of boron per liter, in the soil (sand) solution of thoroughly washed sand either in the form of boric acid, potassium borate, or borax, is capable of entirely stopping germination.

A half century ago Heckel (13) reported the injurious effects of alkali borates on the germination of seed, but the milligram concentration of the soil solution that will prevent germination of soybeans has never before been determined. The data in table 1 show that the seeds vary in their resistance to this injurious element. A few of the seed were able to resist the toxic action of the element in concentrations as high as 200 mgm. per liter of the soil (sand) solution. In all these experiments at least 100 mgm. of boron was capable of reducing materially the percentage germination of the seed. It might well be observed at this time that the percentage germination secured in all the check tests, 82.5 per cent, was very good for soybeans. The weaker concentrations of boron appear to delay germination. It was observed that, for the first few days after the seedlings began to appear at the surface of the sand, 10 mgm. of boron per liter of soil solution was capable of delaying germination.

Many investigators have noted this retarding effect of boron compounds on the germination of seeds, particularly under field conditions. Voelcker (24) has noted this effect of boric acid and borax on wheat and barley. This same influence of borax on cotton has been reported by Blackwell and Collings (5) and by Skinner and Allison (22), on cotton and corn by Sherwin (21), on corn and potatoes by Blair and Brown (6) and by Neller and Morse (19). Archangeli (3) tested the influence of boric acid on germination by soaking a large number of species of seeds in concentrations of boric acid containing about 1773, 886, and 443 mgm. of boron per liter respectively. He reported that 1773 mgm. prohibited germination altogether, and that the other concentrations delayed germination in proportion to the concentration. In 1892 Morel (18) concluded that boric acid and borax when used in equal quantities, equally diminished or inhibited the germination of kidney beans and wheat when the seed were soaked in solutions of each.

This latter conclusion is not upheld by the results of this work with soybean seed. Observation and a careful study of table 1, indicate that in their action on germination boron compounds are not equal when used quantitatively, but that they are about equal when compared on a boron content basis.

In these germination experiments wherever as much as 10 mgm. of boron was applied per liter of soil (sand) solution the edges of the young leaves were tinged yellow; with the higher concentrations of boron the entire seedlings were chlorotic. Warington (25) called attention to a similar condition with the broad bean, but she observed that the condition appeared to be overcome with further growth of the plants.

Experiments conducted in soil

It has been noted by many that under field conditions the injury to field crops from borax-carrying fertilizers is greater in sections where the soils are sandy. This, as has been pointed out by Cook and Wilson (11), is probably due to the absorption of the boron by the colloidal material of the heavier soils, or to a chemical conversion of the soluble boron compounds into insoluble ones. In order to determine the extent of this fixation of boron, a germination experiment was made on Sassafras loam soil. Borax was used as the carrier of boron. Table 1 gives the results of this experiment also. These data show that a minimum equivalent of about 500 mgm. of boron per liter of soil solution materially inhibited seed germination in soil. A minimum of 250 mgm. of boron produced an unhealthy appearance in the seedlings. Germination was not entirely prevented by 1000 mgm. of boron per liter of soil solution. A comparison of these results with those secured with washed sand, indicates considerable dilution of the boron through absorption or chemical combination.

A close examination of the seed that failed to come up revealed that the growing point of the plumule had been killed. Where 1000 mgm. of boron was present in the soil solution of the experiments conducted in sand, practically no development of the plumule had taken place, but with the weaker concentrations of boron, the plumule showed greater development. Likewise, the extent of growth was found to be correlated with the concentration of the boron. The development of the root systems of the seedlings in the pans receiving 10 mgm. and more of boron was diminished by increasing the concentration of boron.

It is not known just what physiological effect boron has on the germinating seed, or on the young seedling. Schreiner et al. (20) have suggested that the element may interfere in some way with the liberation of sugars. They call attention to the fact that borax is capable of forming a chemical union with sugar alcohols, such as mannite. It is upon this combination that one of the present methods of determining borax is based.

A brown incrustation was noticed on the surface of all pans of sand, and a gray incrustation on all pans of soil receiving 500 mgm. or more of boron per liter. Warington (25) made a similar observation when 4 gm. of boric acid was added to 22.5 pounds of soil. She suggested that this was due to a surface concentration of the boron compounds. This suggestion is probably correct, for in the experiments reported in this paper where washed sand was used, no other soluble matter could have been present.

THE INFLUENCE OF BORON ON SOYBEANS GROWN IN SAND

After the sand had been weighed into the pots and the fertilizer added, the young seedlings were transplanted to the pots and a few days later solutions of the boron compounds were added to each culture.

Six series of nine cultures each were run. These will be designated as Boric

Acid Series I and II, Potassium Borate Series I and II, and Borax Series I and II. Anhydrous borax or the borax equivalent of boric acid or of potassium borate, was applied on an acre basis. As the moisture was maintained at 12.5 per cent, the concentration of boron in the soil (sand) solution could be determined. The applications of boron varied from 1 to 75 pounds per acre, or the equivalent of 0.46 to 34.53 mgm. per liter of the soil (sand) solution. The individual applications on a pound per acre basis, and on a milligram of boron per liter of soil (sand) solution basis, are given in table 2.

Toxicity of boron as shown by visible injury to the leaves

Within from three to five days after the boron had been added, visible injury occurred on all plants receiving an initial application equivalent to 10 pounds or more of borax per acre. An application of 10 pounds of borax per acre

TABLE 2

Cultures showing boron injury on the leaves of plants grown in seashore sand

AMOUNT OF BORAX OR EQUIVALENT PER ACRE	AMOUNT OF BORON PER LITER OF SOIL SOLUTION	TIME ELAPSING BETWEEN APPLICATION OF BORON COMPOUND AND APPEARANCE OF INJURY					
		Boric Acid Series		Potassium Borate Series		Borax Series	
		I	II	I	II	I	II
pounds	*mgm.*	*days*	*days*	*days*	*days*	*days*	*days*
0	0						
1.0	0.46	17	17	21	21	17	17
2.5	1.15	10	10	10	10	11	11
5.0	2.30	9	9	9	9	10	10
7.5	3.45	9	9	6	6	9	9
10.0	4.60	6	6	5	5	5	5
25.0	11.51	4	4	4	4	4	4
50.0	23.02	3	3	4	4	3	3
75.0	34.53	3	3	3	3	3	3

produces a concentration of boron in the soil (sand) solution—provided none is fixed—of 4.6 mgm. per liter of cultural solution. Table 2 also gives the number of days elapsing between the application of the boron compound and the appearance of injury in the boric acid, potassium borate, and borax series. It will be observed that the visible injury to the leaves occurred almost simultaneously in the boric acid, potassium borate, and borax series. Furthermore, the injury to the leaves appeared practically simultaneously in all cultures receiving the same application of boron. In all six series that received more than 50 pounds of borax, or its equivalent per acre, all plants were killed within a week after the application of the boron compounds. The plants of these cultures did not show very clearly the characteristic leaf injury. The concentration of the toxic element was apparently so great in these cultures that the entire plant turned chlorotic and died within a short time. This

was also observed later when large applications of boron were made in the water culture experiments. Wherever 25 pounds of borax per acre was applied, the plants were nearly dead when harvested. The injury appeared consecutively from higher to lower applications until an application of 1 pound per acre, or the equivalent of 0.46 mgm. of boron per liter of soil (sand) solution, produced the toxicity on the leaves. No application lower than 1 pound per acre was made. The extent of the visible injury was about the same in all cultures receiving the same applications of boron, whether in the form of boric acid, potassium borate, or borax. All cultures receiving more than 7.5 pounds of borax per acre or 3.45 mgm. of boron per liter of soil (sand) solution, showed a correlated stunting of the plants with an increase in the application of the boron compound.

TABLE 3

Dry weight per plant of tops of soybeans grown in seashore sand

POT	AMOUNT PER ACRE OF BORAX OR EQUIVALENT	DRY WEIGHT PER PLANT OF SOYBEAN TOPS FOR*		
		Boric Acid Average Series I and II	Potassium Borate Average Series I and II	Borax Average Series I and II
	pounds	*gm.*	*gm.*	*gm.*
1	0	1.6361	1.6313	1.2797
2	1.0	1.1366	1.5321	1.3459
3	2.5	1.5450	1.6553	1.1566
4	5.0	1.4399	1.5760	1.4655
5	7.5	1.2454	1.5254	1.2733
6	10.0	1.3476	1.5171	1.1587
7	25.0	1.1087	0.9760	1.1449
8	50.0	0.5068	0.5348	0.4910
9	75.0	0.2619	0.2491	0.3102

* Average of six plants.

The influence of boron on the dry weights of plants grown in sand

The plants were harvested at the end of their seedling phase of growth. The roots were not harvested. Table 3 shows that boron in any form has a very harmful influence on the dry yield of plant tops. The dry weight per plant was reduced by as low an application as 1 pound of boric acid per acre; by 5 pounds or more of potassium borate; and by 7.5 pounds or more of borax. However, the 1.0 pound application of potassium borate and the 2.5 pound application of borax produced less dry matter than their respective checks.

The dry weights of these six series again corroborate the conclusions secured with the germination test: first, that the borate ion produces the injury; and, second, that compounds of boron are toxic in proportion to the boron they carry, and such compounds are comparable on that basis. It is apparent that the amount of absorption of boron is very small in pure sand, for injury was secured here with 0.46 mgm. of boron per liter of soil (sand) solution.

The stimulating influence of boron

There was no evidence from any of the six series that boron is essential or stimulating to the growth of soybeans. The average dry weights of all duplicate series (table 3) reveal only three cases where the dry weights are greater than that of the check—where 1 and 5 pounds of borax, respectively, and where 2.5 pounds of potassium borate were added.

THE INFLUENCE OF BORON ON SOYBEANS GROWN IN SOIL

Since most of the boron injury reported from borax-carrying fertilizers used under field conditions was obtained on sandy types of soil of the Coastal Plain, it was thought best to use a representative Coastal Plain soil—Norfolk sand—for this study. It was also believed that with this class of soil the effect of small applications of boron on plant growth would be more pronounced than with a heavier type of soil.

TABLE 4

Cultures showing boron injury on the leaves of plants grown in Norfolk sand

AMOUNT OF BORAX OR EQUIVALENT PER ACRE	AMOUNT OF BORON PER LITER OF SOIL SOLUTION	TIME ELAPSING BETWEEN THE APPLICATION OF BORON COMPOUND AND APPEARANCE OF INJURY					
		Boric Acid Series		Potassium Borate Series		Borax Series	
		III	IV	III	IV	III	IV
pounds	*mgm.*	*days*	*days*	*days*	*days*	*days*	*days*
0	0						
1.0	0.46	22	22	20	20	22	22
2.5	1.15	10	10	10	10	16	16
5.0	2.30	9	9	9	9	7	7
7.5	3.45	7	7	8	8	7	7
10.0	4.60	6	6	5	5	6	6
25.0	11.51	4	4	4	4	5	5
50.0	23.02	3	3	3	3	5	5
75.0	34.53	3	3	3	3	5	5

As in the previous study, six series of nine cultures each, were run in this test. These series are designated as Boric Acid Series III and IV, Potassium Borate Series III and IV, and Borax Series III and IV. The same amounts of soil, and the same applications of fertilizer were used as in the experiments with seashore sand.

Toxicity of boron as shown by the visible injury to the leaves

Visible injury to the leaves again occurred in all the cultures of all the series receiving boron. In table 4 is given the number of days elapsing between the application of the boron compound and the appearance of injury. It will be observed that the visible injury occurred in the six series in about the same

length of time. Again, the same concentration of the borate ion appeared to produce the same results, regardless of the carrier.

Tables 2 and 4 show that the results secured with Norfolk sand are similar to those secured with pure sand. In all cases 1-pound applications of borax, or its equivalent, were sufficient to produce visible injury on the leaves. This soil was a coarse sand and carried only small amounts of clay. It is, therefore, not surprising that the results are closely correlated to those secured with pure sand.

Special attention is directed to the small amounts of boron capable of producing visible injury. Although considerable work has been done in pot cultures in connection with field experiments by many investigators, few have indicated that less than 5 pounds per acre of borax was toxic to any plant even when the material was applied in the drill. This is probably because the first

TABLE 5

Dry weight per plant of tops of soybeans grown in Norfolk sand

POT	AMOUNT PER ACRE OF BORAX OR EQUIVALENT	DRY WEIGHT PER PLANT OF SOYBEAN TOPS* FOR		
		Boric Acid Average Series III and IV	Potassium Borate Average Series III and IV	Borax Average Series III and IV
	pounds	*gm.*	*gm.*	*gm.*
1	0	1.3841	1.0776	1.1205
2	1.0	1.0200	1.0075	1.8366
3	2.5	0.9610	0.9171	1.0694
4	5.0	0.9057	0.8375	1.0295
5	7.5	0.9432	0.8582	0.9358
6	10.0	0.9156	0.7072	1.0208
7	25.0	0.5600	0.5434	0.6650
8	50.0	0.2983	0.2103	0.4101
9	75.0	0.2864	0.2298	0.2129

* Average of six plants.

appearance of the injury was not readily recognized. It has been observed frequently in these experiments that a plant might appear perfectly sound to a casual observer, and yet upon a close inspection the presence of the visible toxicity on the leaves could be noted. It was also observed that many of the lower leaves of the plant may show the injury, and yet the dry weight of the plant may not be reduced materially.

It is very probable that had a ½-pound application of borax been made and had the plants been allowed to grow to maturity, toxic injury to the leaves would have appeared before harvesting.

The influence of boron on the dry weights of plants

The average dry weights of all duplicate series are given in table 5. These data show that an application of 1 pound of borax per acre in the form of

boric acid or potassium borate, or of 2.5 pounds per acre in the form of borax, is sufficient to decrease the dry weights below that of the controls during the seedling phase of growth.

The stimulating influence of boron

There is no indication in any soil series of any marked stimulation to soybeans, although as many as 162 plants were grown in these six series. On the other hand, Voelcker (24) has reported a slightly stimulating effect on wheat with quantities of borax not exceeding 27 pounds per acre, and Breckenbridge (7) grew in pots potatoes which appeared to be stimulated with 4 to 6 pounds of borax per acre.

It should not be overlooked that boron compounds are somewhat antiseptic, and that a certain amount of soil sterilization may take place. This action of boron may influence the soil organisms, and thus have an indirect influence on plant growth.

THE INFLUENCE OF BORON ON THE SEEDLING PHASE OF GROWTH OF SOYBEANS IN WATER CULTURES

Although many investigators have reported boric acid and borax to be toxic to plants, very little exact work has been done to determine at what minimum concentrations the toxic compounds will produce the harmful effects. Most of the work that has been reported has been conducted under field conditions. Many investigators have called attention to the fact that where toxic compounds are applied under field conditions various factors may enter in to obscure the results. For example, the amount and distribution of rainfall may alter the concentration of the soil solution and, therefore, influence the relative toxicity of the compound. Even where toxic compounds are applied to soil in pots, and the pots kept under controlled greenhouse conditions, absorption of the toxic compound will take place to an extent depending upon the physical and chemical nature of the soil. This absorption will, in turn, influence the concentration of the toxic element in the soil solution, and thus vary the extent of injury to the plant.

This being true, it naturally follows that water culture tests, rather than pot or field tests, offer the best possible means of studying under controlled conditions the harmful and beneficial influences of minute quantities of chemical compounds upon the growth processes of any plant, provided the plant in question can be grown successfully in nutrient solutions. It was with this idea in mind that this phase of the study was undertaken.

The soybean was used for this study because legumes are more sensitive to toxic compounds than are non-legumes, and because it has proved so well adapted to nutrient solution work under greenhouse conditions. Cook (10) has reported that legumes are more sensitive to boron compounds than non-legumes. The Modified Tottingham solution was used in all the nutrient solu-

tion work because Jones and Shive (15) have reported favorable results when growing soybeans in this solution.

Several investigators have reported the toxic influence of soluble boron compounds on the growth of seedlings. Archangeli (3), for instance, found that seedlings of maize, white lupines, vetch, or wheat placed in a solution of boric acid containing about 1773 mgm. of boron per liter of solution were killed, but that they were less severely injured with weaker concentrations. Likewise, Kahlenburg and True (16), limiting their experiments to from fifteen to twenty hours duration, found that seedlings of lupines put into a solution of boric acid containing about 440 mgm. of boron per liter were killed, concentrations of 220 mgm. of boron per liter left the plants apparently just alive, and a weaker concentration of 110 mgm. produced no injurious influence.

At the beginning of this experiment it was thought probable that any harmful or beneficial influences of boron compounds on soybeans grown in nutrient solution would appear in the early stages of growth. It was also thought probable, that if these influences should manifest themselves when the plants were young, they might be obscured by further growth of the plant. A study was first made, therefore, of the influence of boron compounds on the growth of soybean plants during their seedling phase. A comparative study was also made of the influence of boron in the form of boric acid, potassium borate, and borax.

As no investigator had worked on this problem with the soybean when grown in the Modified Tottingham nutrient solution, it was found necessary first to apply boron to the culture solutions over a wide range of concentrations, and to determine whether any noticeable effects could be produced. Therefore, a series of fifteen cultures receiving boric acid was run and harvested 21 days later when the plants were in full bloom. Boric acid was applied in concentrations ranging from 0.006 to 55.89 mgm. of boron per liter of the nutrient solution. The individual concentrations are given in table 6.

Toxicity of boron as shown by visible injury to the leaves

Five days after the application of the boric acid, small dark brown spots began to appear on the first pair of leaves of culture 15—this culture had received 55.89 mgm. of boron per liter of the nutrient solution. The injury, which was very pronounced, was apparently of the same type as that observed on plants grown in sand and soil containing boron-carrying fertilizers. This injury appeared within three days, consecutively in the next five cultures receiving lower concentrations of boron, and was produced by all applications of more than 0.44 mgm. of boron. It is evident that boron in the form of boric acid in nutrient solution is toxic to soybean seedlings, and that the extent of this toxicity is dependent upon the concentration of boric acid. It was also observed that the appearance of this visible injury on the leaves occurred simultaneously and uniformly on all plants of each culture.

After securing these results, another series, designated as Boric Acid Series VI, was started to determine whether an application of boron as boric acid, in

concentrations ranging between 0.44 and 0.89 mgm., would produce the injury during the same growth period. Visible toxicity to the leaves again appeared. Table 6 also shows the concentrations of boron used in all cultures of this series,

TABLE 6

Amount of boron applied per culture and time elapsing between the application of boron compounds and the appearance of the injury

CULTURE	BORIC ACID SERIES V		BORIC ACID SERIES VI	
	Boron per liter of nutrient solution	Time required for injury to appear	Boron per liter of nutrient solvent	Time required for injury to appear
	mgm.	*days*	*mgm.*	*days*
1	0		0	
2	0.006		0.22	
3	0.013		0.33	
4	0.027		0.44	
5	0.055		0.53	21
6	0.110		0.62	
7	0.220		0.71	20
8	0.440		0.80	19
9	0.890	17	0.89	19
10	1.740	7	1.07	17
11	3.490	7	1.25	17
12	6.980	6	1.43	14
13	13.970	6	1.60	14
14	27.940	5	1.74	13
15	55.890	5	3.49	11
CULTURE	POTASSIUM BORATE SERIES V		POTASSIUM BORATE SERIES VI	
	Boron per liter of nutrient solution	Time required for injury to appear	Boron per liter of nutrient solution	Time required for injury to appear
	mgm.	*days*	*mgm.*	*days*
1	0		0	
2	0.002		0.28	
3	0.004		0.43	21
4	0.009		0.56	19
5	0.018		0.67	19
6	0.036		0.79	17
7	0.072		0.90	19
8	0.140		1.01	14
9	0.280		1.12	14
10	0.560		1.35	14
11	1.120	17	1.58	14
12	2.250	7	1.80	14
13	4.510	7	2.03	14
14	9.030	6	2.25	13
15	18.060	5	4.51	10

the cultures on which the injury occurred, and the time elapsing between the application of the boron compound and the appearance of the injury on the

leaves. It will be observed that at the time this series was harvested, visible injury to the leaves had been produced where only 0.53 mgm. of boron had been applied per liter of the nutrient solution, and that injury had not occurred where 0.44 mgm. of boron had been applied. These results corroborate as closely as could be expected the results secured with Boric Acid Series V.

Simultaneously with Boric Acid Series V and VI, two similar series were run with potassium borate as the carrier of boron. The concentrations of boron, and the time elapsing between the application of the boron compound and the appearance of the injury on the leaves are given in table 6. Again a similar visible injury occurred in those cultures receiving a high dose of boron. It thus appeared that boron, either in the form of boric acid or potassium borate, was capable of producing the injury. At harvest time, the highest applications of boron in this series which had not showed the injury was 0.56 mgm. Potassium Borate Series VI was then run with a smaller variation in the concentrations of boron. Table 6 shows that the lowest concentration producing injury during this test was 0.43 mgm. This slight variation from the results secured in Potassium Borate Series V might be due to the differences in the environmental factors during the periods when the two series of cultures were grown.

It is interesting to note that the lowest concentration of boron in the form of boric acid producing injury during the seedling phase of growth (0.53 mgm.) is very nearly the same as in the potassium borate series (0.43 mgm.). It thus appears that the borate ion produces the visible injury, and that the time required is correlated with the amount of boron present in the culture solution. The absorption of enough boron to produce visible injury on the leaves takes place in less time from the cultures containing the higher concentrations of boron.

Relative influence of boron in the form of boric acid, potassium borate, and borax on visible injury

In order to compare the relative influence of boron in various forms, a series of duplicate cultures was run to determine the time required for the injury to appear, and the relative degree of the injury at any given time in cultures to which the same amounts of boron had been added in the form of boric acid, potassium borate, and sodium borate or borax. The concentration of boron used in all cultures was 3 mgm. per liter of nutrient solution. The plants were grown in sand in percolators to which a continual renewal of the nutrient solution was made.

In this series the injury occurred on all plants simultaneously, both on the first and second pairs of leaves. These results again show that the borate ion produced the toxicity. The extent of the injury, after its appearance up to the time of harvesting, was apparently the same on all plants at all times. Plate 1 shows the type and the extent of the injury at harvest time on the first pair

of leaves of representative plants which received boric acid, potassium borate, and borax, respectively.

The influence of boron on the development of the root system

Warington (25) and Agulhon (1) have reported that some concentrations of boron, added in the form of boric acid to the water cultures, markedly injured, and others stimulated the root systems of plants. In the five series of plants under discussion no visible injury to the root system could be detected at any time except when the application of boron was so great that it killed, or retarded, the growth of the entire plant. In such cases the root systems of the injured plants were smaller, but in other respects similar to those not receiving boron.

The stimulating influence of boron

Agulhon (1) secured an increase in dry weight of wheat plants when boric acid was applied in small quantities ranging from 0.5 to 10.0 mgm. of boron per liter of synthetic culture solution. Boric Acid Series V showed some evidence of stimulation when either the green or the dry weights of tops, roots, or total plant were compared. This evidence, however, was not present in Boric Acid Series VI or in Potassium Borate Series V and VI. The dry weights of these three series showed only normal variations. In no case was there any visible evidence during the seedling phase of growth of any stimulation to the roots or tops due to boron, either in the form of boric acid or of potassium borate. The plants in all control cultures appeared to be perfectly normal.

THE INFLUENCE OF BORON ON SOYBEANS GROWN TO MATURITY IN SOLUTION CULTURES

An analysis of the data already given on the influence of boron on the seedling growth of soybeans indicated that had harvesting been delayed beyond the flowering period, or had the plants been grown to maturity, smaller concentrations of boron than 0.4 or 0.5 mgm. per liter of cultural solution would have produced injury. In order to determine whether this were true, two series of fourteen cultures each were started to which boron in the form of boric acid was added, and three series of fourteen cultures each to which boron in the form of borax was added. It was also desired to determine whether there were any stimulating effects in the advanced phases of growth of the plant, as no marked stimulation had been shown during the seedling phase.

In all of these series the constant renewal method of solution change, as previously described, was employed. The plants of Borax Series IX were grown in sand in percolators. The concentration of boron was so arranged that the lowest producing toxicity during the seedling phase of growth was placed about midway in the series. It was thought that if any stimulating

influence was present it would show itself at a concentration just below or just above that which produced the appearance of the visible injury on the leaves.

Boron was applied to the five series in concentrations ranging from 0.01 to 2.50 mgm. per liter of the cultural solution. The individual applications of boron per culture are given in table 7.

TABLE 7

Cultures showing boron injury on the leaves when plants were grown to maturity

CULTURE	BORON PER LITER OF NUTRIENT SOLUTION	TIME ELAPSING BETWEEN THE APPLICATION OF BORON COMPOUND AND APPEARANCE OF INJURY FOR			
		Boric Acid Series		Borax Series*	
		VII	VIII	VII	VIII
	mgm.	*days*	*days*	*days*	*days*
1	0				
2	0.01				
3	0.05				
4	0.10				46
5	0.20	31	37	42	40
6	0.30	29	26	39	39
7	0.40	24	26	38	38
8	0.50	28	24	33	34
9	0.60	22	22	25	25
10	0.70	18	18	21	21
11	0.80	17	17	22	21
12	0.90	16	15	20	20
13	1.00	16	16	19	19
14	2.50	11	11	13	13

* Borax Series VII and VIII were run at a different time from Boric Acid Series VII and VIII.

Toxicity of boron as shown by visible injury to the leaves

The same injury noticed during the seedling stage of growth, when boric acid and potassium borate were applied, was noted in all five of these series where boric acid and borax were applied. In about one and a half to two weeks after the application of the boron, injury appeared on the leaves where 2.5 mgm. had been applied. A few days later the injury occurred where 1.0 mgm. had been applied, and from this time on until harvest the injury appeared in successive lower concentrations in all the series. In about four or five weeks the injury had appeared in cultures receiving 0.5 mgm. of boron. In about seven weeks the injury had occurred where as low as 0.2 mgm. of boron had been applied. The plants were harvested at maturity, when they were eight weeks old. The lowest application in Boric Acid Series VII and VIII and in Borax Series VII showing the injury was 0.2 mgm. In Borax Series VIII

and IX, 0.1 mgm. of boron showed the injury. It will be observed that down to a concentration of about 0.6 mgm. the injury in all series occurred simultaneously.

Special attention is directed to the very small quantities of boron that are capable of producing the visible injury on the leaves—particularly small when compared with other substances, such as arsenic and copper salts, which are generally considered poisonous to plants. Hotter (14) has observed that the leaves of peas and maize were injured by applications of boric acid. He was able to detect injury with the equivalent of 1.7 mgm. of boron per liter of nutrient solution, which is about seventeen times as great as that found in this experiment.

Relative influence of boron in the form of boric acid and of borax

Hotter (14) has also reported that weight for weight, borax is less toxic than potassium borate, which in turn is less toxic than boric acid. The results secured in Boric Acid Series VII and VIII, and Borax Series VII, VIII, and IX confirm the results of Hotter. Borax carries less boron than potassium borate, which in turn carries less than boric acid. The data given in the tables reported in this group of experiments, where the plants were grown to maturity, indicate that boron compounds are toxic in proportion to the boron they carry. These data uphold the conclusions drawn from a comparison of the three boron compounds in the study of the seedling phase of growth of the soybean. On the other hand, Hazelhoff (12) working with corn, beans, and oats, found that injury increased faster with borax than with boric acid. Voelcker (24) has also reported more marked injury with borax than with boric acid.

Description of the visible injury on the leaves

The visible boron injury on the leaves of soybeans is very characteristic and is not easily confused with other forms of toxicity, such as injury due to an excess of iron. It appears that the boron is continually being absorbed, and that very high concentrations cause the plant to turn yellow and die, but that lighter doses concentrate in the rapidly growing cells near the margin of the leaf, and cause their death. The injury may be noted first by the appearance of light colored, partly chlorotic tissue about two to three centimeters on each side of the leaf tip. These affected areas develop a day later into characteristic dark brown spots. An examination of these spots under the microscope shows that the largest number of dark injured cells, which later become transparent, are adjacent to the very small veins. These spots usually originate about one-fourth of a centimeter from the edge of the leaf. (See Plate 1.) They never occur on the cotyledons, as is sometimes the case with other toxic conditions. With further development of the toxicity, spots may appear in the center of the leaf, but they always occur between the larger veins. It was also observed that these spots do not increase to much larger than half a centimeter in diame-

ter, and do not readily cross the larger veins. The dying of the tissue, particularly when the leaves are young, causes the edges to roll either up or down. The injured leaf may otherwise appear to be in a healthy condition until about one-half of the surface area of the leaf becomes affected; the leaf then turns yellow and drops from the plant. This shedding of the leaves, which was very noticeable in Boric Acid Series VII and VIII, probably removes from the plant considerable amounts of the toxic element. Whether this is of any particular value to the plant is questionable. It would appear improbable, however, that once the toxic ion has been fixed in a group of cells in sufficient quantities to produce death it would again become soluble, and therefore toxic

TABLE 8

Average dry weight per plant of soybeans grown to maturity and nutrient solution

CULTURE	BORON PER LITER OF NUTRIENT SOLUTION	*BORIC ACID AVERAGE SERIES VII AND VIII	*BORAX AVERAGE SERIES VII AND VIII
	mgm.	*gm.*	*gm.*
1	0	8.5511†	5.7359
2	0.01	9.8400	7.6399
3	0.05	9.3105	6.7854
4	0.10	9.2083	6.5507
5	0.20	11.4770	6.1656
6	0.30	8.8055	7.8172
7	0.40	12.0458	9.0106
8	0.50	11.1057	7.7616
9	0.60	10.6501	7.4355
10	0.70	10.5321	8.8039
11	0.80	8.7565	6.6379
12	0.90	10.5011	5.9596
13	1.00	12.1673	8.6100
14	2.50	12.2756	8.3490

* Borax Series VII and VIII were run at different periods from Boric Acid Series VII and VIII. Average of six plants.

† Average of three plants.

to other cells. Although the injury to the leaves gradually works its way up the plant, it never appears on the young, rapidly growing tissue.

The influence of boron on the development of the root system

A careful examination from time to time of the root systems of all series of plants grown in water culture showed no difference in any of the cultures. This confirmed the results which have been noted previously in the study of the seedling phase of growth, and is directly contrary to the results secured by Warington (25) with the broad bean at the Rothamsted Station.

The influence of boron on the dry weights of plants

The average dry weights of the plants of Boric Acid Series VII and VIII are given in table 8. It was observed, although the figures are not given here,

that only three cultures of the two series had a dry weight at maturity lower than the controls. Certainly the toxic influence of boron at any of the concentrations used was not sufficient to injure the plant materially. In most cultures there was a material increase of dry weight over that of the controls.

The average dry weights of the total plants of Borax Series VII and VIII, which are also given in table 8, show an increase over the checks for the cultures receiving boron. Only one culture of Borax Series VII and VIII showed a dry weight less than the control.

In most of the work previously reported, the dry weights of plants have been taken as the index of toxicity. The results of these experiments indicate that boron is toxic in lower concentrations than is necessary to reduce the dry weight, and that the visible injury to the leaves is by far a superior method of indicating harmful effects on plant growth.

The stimulating influence of boron

The data in table 8 give the first marked indication, so far observed, that boron may be stimulating to plant growth. This stimulation is noticeable in both the boric acid and the borax series. The greatest individual dry weight in the boric acid series was secured with the highest concentration of boron applied (2.5 mgm.) although this plant suffered the greatest from toxicity, as indicated by the visible injury to the leaves. The increase over the controls in the dry weight of all cultures receiving boron appears to be correlated with the increase of boron in the nutrient solutions, but the correlation is not very uniform. This also appeared to be true where borax was applied.

Concentrations of 0.014 to 7.09 mgm. of boron per liter of nutrient solution appeared to be beneficial. It is well to emphasize that in all of the series reported in this paper, cultures containing as low a concentration of boron as 0.01 mgm. per liter of nutrient solution were included. With one exception, all control plants of all cultures appeared to be normal healthy plants, and showed no characteristic dying, as noted at Rothamsted. Of course, it may be that the soybean is not influenced by boron as is the broad bean. Warington (26) did not secure the same results with barley as she did with the broad bean. Agulhon (1) is inclined to believe that boron is "a particular element" and that it may be required by particular groups of plants.

The influence of boron on the shoot-root ratio

Warington (25) found a decided drop in the shoot-root ratio of the broad bean in all cultures where the concentration of boric acid was favorable to plant growth. In those cultures where boron exerted a toxic influence, the ratio rises to about the same level as in the controls. Agulhon (1) has also noted a similar drop in the shoot-root ratio of wheat plants when grown in water culture solutions. Warington (25), however, could find no definite relationship between the shoot-root ratio of variously treated barley plants.

The shoot-root ratios of soybeans grown in the two Boric Acid Series VII and VIII, and of the two Borax Series VII and VIII were determined. It was observed from these data that no definite relationship can be shown between the shoot-root ratios of the variously treated cultures. It thus appears that the root and shoot of the soybean must be affected about equally by the boron compound.

The influence of boron on the absorption of mineral elements

Agulhon (1) and Warington (25) have both found an increase in the green weight value of plants with certain concentrations of boron. Agulhon (1) attributed this to an increase in the water-holding capacity of the plant, resulting from a state of over-mineralization induced by the absorption of boron. It was thought that if this were true, the percentage of ash of the various cultures would show this influence. Ash determinations, therefore, were made of Borax Series IX. These data showed that there is no relationship whatever between the concentration of boron in the nutrient solution and the amount of mineral elements absorbed.

SUMMARY

This piece of research was attempted in order to determine what influence boron exerts upon the growth of soybeans. Experiments were run to determine the influence of boron on the germination of seeds and on the growth of soybeans grown in nutrient solution, sand, and soil. A comparative study was also made of the influence of boron when applied in the form of boric acid, potassium borate, and sodium borate or borax.

A total of 78 germination tests were made. In addition, 136 nutrient solution cultures, 54 sand cultures, and 54 soil cultures were grown. Altogether 732 plants were grown to test out the influence of boron on plant growth. In some of the experiments the plants were harvested when they had reached their flowering stage, whereas in other experiments the plants were grown to maturity before harvesting. Some of the principal results secured from the study are as follows:

Influence on germination

1. The presence of as much as 250 mgm. of boron per liter in the soil (sand) solution entirely prevents the germination of soybean seed.
2. The presence of as much as 10 mgm. of boron per liter in the soil solution is capable of delaying the germination of soybean seed.
3. The presence of as much as 10 mgm. of boron per liter in the soil (sand) solution had such an influence upon germination that chlorotic, or partly chlorotic seedlings were produced.
4. Sassafras loam soil has the power of absorption of boron, and of reducing the toxic action of boron compounds on germination.
5. The influence of boron on germination appears to be identical whether in the form of boric acid, potassium borate, or borax.

Influence of boron compounds on soybean plants grown in sand

1. Visible injury to the leaves appeared on all cultures where as much as 1 pound of borax, or its equivalent, was added per acre.
2. Boric acid, potassium borate, and borax reduced the dry weight of plants when applied in quantities equivalent to 7.5 pounds, or more, of borax per acre. With potassium borate and boric acid this injury was shown when applications of 5 and 1 pounds, respectively, were made.
3. Equivalent amounts of boron in the form of boric acid, potassium borate, or borax, produced about the same visible injury to the leaves.
4. No marked stimulation to growth could be detected where boron compounds were applied to plants growing in sand.

Influence of boron compounds on soybean plants grown in soil (Norfolk sand)

1. Visible injury to the leaves appeared on all cultures where as much as 1 pound of borax, or its equivalent, was added per acre.
2. All boron compounds tested reduced the dry weight of plants where applied in quantities equivalent to 1 pound of borax per acre.
3. Equivalent amounts of boron in the form of boric acid, potassium borate, or borax, produced about the same visible injury to the leaves.
4. No visible stimulation to growth could be detected where boron compounds were applied to plants growing in soil.

Influence of boron on the seedling phase of growth of plants grown in nutrient solution

1. Boron is toxic to soybeans, and this toxicity manifests itself, where small quantities are present, in the form of a characteristic injury to the leaves; or where large quantities are present, in stunting or killing the plant.
2. During the seedling phase of growth of soybeans, at least 0.4 to 0.5 mgm. of boron per liter of nutrient solution is toxic.
3. The toxic influence of boron is practically the same whether it is in the form of boric acid, potassium borate, or borax.
4. Boron is not necessary to the growth of soybean plants during the seedling stage of growth.
5. No marked indication of any stimulating influence of boron could be observed.

Influence of boron on plants grown to maturity in nutrient solution

1. Boron when present in the nutrient solution in concentrations as low as 0.1 to 0.2 mgm. per liter of the solution is able to produce visible toxicity on the leaves of soybeans.
2. The toxicity of boron is practically the same whether it is added in the form of boric acid or borax.
3. Boron is not necessary to the production of mature soybean plants.
4. Boric acid, and to a lesser degree, borax, exerted a stimulating influence on soybean plants, the greatest stimulation appearing when 2.5 mgm. of boron per liter of cultural solution had been used.

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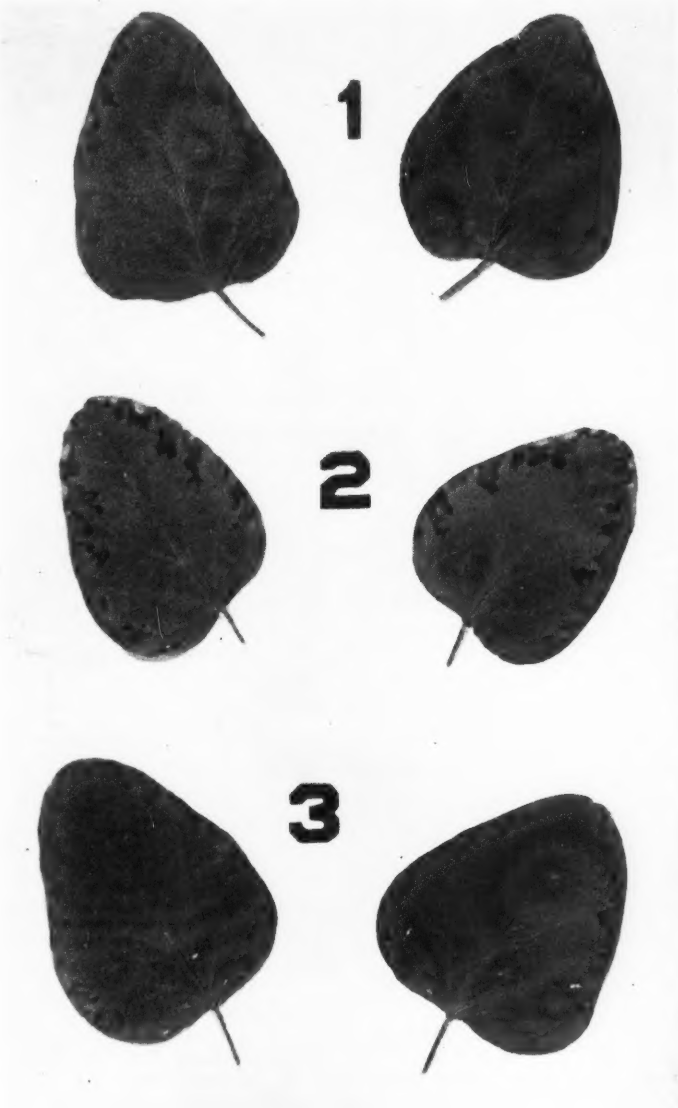
PLATE 1

The Type and the Extent of Boron Injury on the First Pair of Leaves of Representative Plants Which Received Equivalent Quantities of Boron as Boric Acid, Potassium Borate, and Borax

1, Boric acid; *2*, Potassium borate; *3*, Borax


1
2
3

ORGANIC MATTER CHANGES IN TWO SOIL ZONES, AS INFLUENCED BY DIFFERENCE IN FORM, FINENESS, AND AMOUNT OF CALCIC AND MAGNESIC MATERIALS[1]

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It is generally conceded that economic conditions of liming materials are followed by stimulation of bacterial processes. Such processes result in the oxidation of soil organic matter, with the production of nitrates and carbon dioxide. Determinations of residual nitrogen, "humus," and organic CO_2 have therefore been used to measure changes in organic matter. The subject of economic liming and its effect upon conservation of nitrogen and organic matter has been studied in this manner at the Tennessee Station for a number of years. Certain cowpea-wheat rotation experiments (6, 7) and certain cylinder studies (8) that have been reported are being continued. This paper arises from a detached 4-year lysimeter investigation, wherein organic matter changes were incidental to the major objectives of calcium and magnesium outgo, as such outgo was influenced by zone-of-incorporation and by variation in form and amount and degree of fineness of added calcic and magnesic materials.

EXPERIMENTAL

The major variation, that is, zone-of-incorporation, applied in the comparisons among all materials. Hydrated lime at the rate of 2000 pounds of CaO per 2,000,000 pounds of soil, moisture-free basis, was compared with equivalent incorporations of 10–20-, 20–40-, 40–80-, 80–200-mesh and an equal-part composite of limestone and of dolomite, and also with equivalent $CaO-MgO$ incorporations. Three fractional rates of 1000 pounds 500 pounds, and 250 pounds of CaO as $Ca(OH)_2$, were also included.

The experiment extended over the 4-year period, May, 1921 to May, 1925. The lysimeter equipment has been described, together with soil, method of treatment and materials used (4). Originally the entire mass of screened soil was thoroughly mixed to insure uniform composition. One addition was incorporated in the surface half or zone of each tank of one series, without treatment to the lower zone, whereas in another series each addition was incorporated in the lower zone without any treatment to the upper zone. After

[1] The results were obtained by means of equipment donated by the American Limestone Company and through fellowship assistance provided by the National Lime Association.

4 years' exposure to natural leaching, under fallow and without stirring, the two zones were taken up separately and dried. An entire 2-quart sample

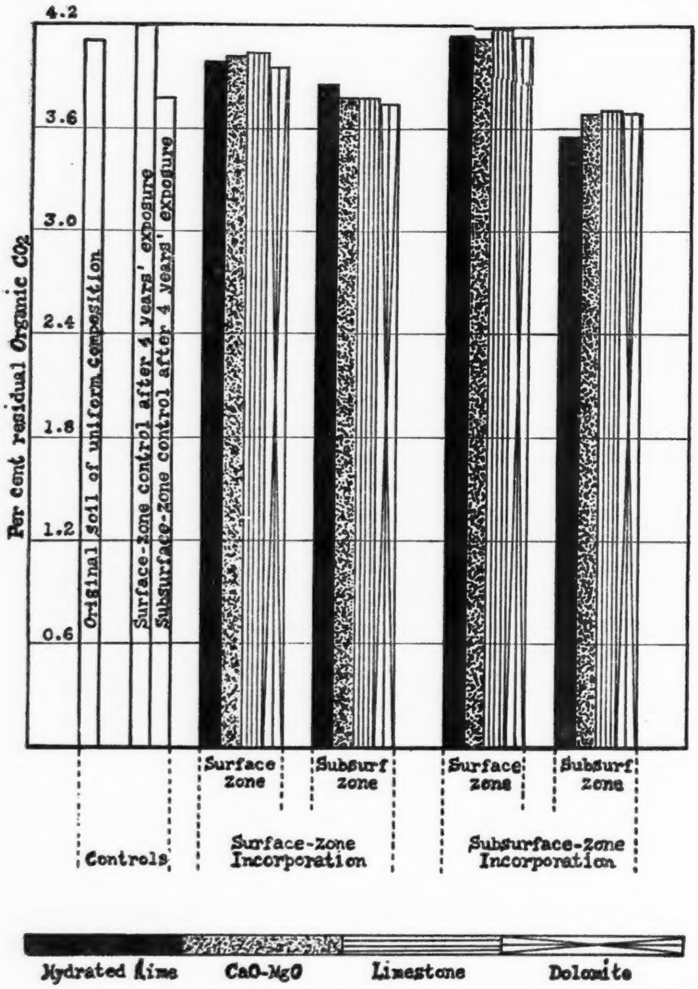

FIG. 1. ORGANIC-CO_2 CHANGES INDUCED IN A LOAM SOIL BY SURFACE-ZONE AND SUBSURFACE-ZONE INCORPORATIONS OF $Ca(OH)_2$, CaO-MgO, 80–100-MESH LIMESTONE AND DOLOMITE AT THE CONSTANT RATE OF 2000 POUNDS OF CaO PER 2,000,000 POUNDS OF SOIL, MOISTURE-FREE BASIS, DURING 4 YEARS' FALLOW EXPOSURE WITHOUT STIRRING

from each zone of each tank was ground to pass a 100-mesh sieve and carbonate-CO_2 was determined upon 100-gm. charges (4). Five-gram charges were

burned in an electric furnace, with precautions to preclude vitiation from volatile sulfur, chlorine, and nitrogen compounds. The total combustion-CO_2 determinations were corrected for the previously reported (4) carbonate-CO_2 results.

TABLE 1

Organic-CO_2 content of two soil zones of an originally uniform soil, as influenced by surface-zone incorporations of caustic and natural forms of calcic and magnesic materials and 4 years' exposure in out-door lysimeters

TANK NUMBER	MATERIALS			ORGANIC CO_2						
	Form	Mesh	CaO ≎ per 2,000,000 pounds of soil	Surface zone			Subsurface zone			Minus variation of sub-surface zone
				A	B	Average	A	B	Average	
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
80[a]	....	......	None	....	....	4.19*	....	....	3.81*	0.38
81[a]	$Ca(OH)_2$	......	250	4.04	4.04	4.04	3.82	3.83	3.83	0.21
82[a]	$Ca(OH)_2$	......	500	4.10	4.12	4.11	3.82	3.84	3.83	0.28
83[a]	$Ca(OH)_2$	......	1,000	4.10	4.16	4.13	3.77	3.79	3.78	0.35
84[a]	$Ca(OH)_2$	......	2,000	3.98	4.00	3.99	3.86	3.86	3.86	0.13
85[a]	CaO-MgO†	......	2,000	4.20	4.20	4.20	3.73	3.74	3.74	0.46
86[a]	CaO-MgO‡	......	2,000	3.87	3.88	3.88	3.82	3.84	3.83	0.05
88[a]	Limestone	10–20	2,000	4.05	4.05	4.05	3.87	3.89	3.88	0.17
89[a]	Limestone	20–40	2,000	4.01	4.02	4.02	3.82	3.81	3.82	0.20
90[a]	Limestone	40–80	2,000	4.05	4.03	4.04	3.83	3.81	3.82	0.22
91[a]	Limestone	80–200	2,000	4.05	4.04	4.05	3.78	3.80	3.79	0.26
87[a]	Limestone	Comp.	2,000	3.97	3.98	3.98	3.78	3.77	3.78	0.20
93[a]	Dolomite	10–20	2,000	4.11	4.11	4.11	3.79	3.76	3.78	0.33
94[a]	Dolomite	20–40	2,000	4.04	4.05	4.05	3.88	3.84	3.86	0.19
95[a]	Dolomite	40–80	2,000	4.04	4.06	4.05	3.86	3.84	3.85	0.20
96[a]	Dolomite	80–200	2,000	3.94	3.96	3.95	3.74	3.76	3.75	0.20
92[a]	Dolomite	Comp.	2,000	4.05	4.06	4.06	3.81	3.82	3.82	0.24
Average						4.05			3.81	0.24

* Average of 6 determinations.

† Burnt dolomite 46.53 per cent CaO and 32.85 per cent MgO.

‡ Mixture of separately calcined oxides.

DISCUSSION

The organic-CO_2 data are given in tables 1 and 2 and condensed in graphic comparisons for the 2000-pound treatments in figure 1.

Before results are discussed, it should be emphasized that the full rates of treatment were incorporated with one-half the entire mass of soil, so that the maximum rate of 2000 pounds CaO-equivalence per 2,000,000 pounds of soil,

or a percentage of 0.1 on the basis of the full depth of soil, was actually a rate of 2000 pounds per 1,000,000 pounds of soil, or a percentage of 0.2 when considered on the basis of direct contact of the additions with one-half of the entire soil mass. In previous studies (3) the same soil received incorporations of burnt and hydrated limes and precipitated $CaCO_3$, at the rate of 4000

TABLE 2

Organic-CO_2 content of two soil zones of an originally uniform soil, as influenced by subsurface-zone incorporations of caustic and natural forms of calcic and magnesic materials and 4 year's exposure in out-door lysimeters

Tank number	Materials: Form	Materials: Mesh	Materials: CaO ≏ per 2,000,000 pounds of soil	Organic CO_2: Surface zone A	Surface zone B	Surface zone Average	Subsurface zone A	Subsurface zone B	Subsurface zone Average	Minus variation of subsurface zone
				per cent	per cent	per cent	per cent	per cent	per cent	per cent
80B	....	......	None	....	....	4.19*	3.77	3.78	3.78*	0.41
81B	$Ca(OH)_2$	......	250	4.26	4.23	4.25	3.77	3.78	3.78	0.47
82B	$Ca(OH)_2$	......	500	4.20	4.17	4.19	3.73	3.69	3.71	0.48
83B	$Ca(OH)_2$	......	1,000	4.06	4.10	4.08	3.70	3.72	3.71	0.37
84B	$Ca(OH)_2$	......	2,000	4.14	4.13	4.14	3.54	3.58	3.56	0.58
85B	CaO-MgO†	......	2,000	4.09	4.08	4.09	3.62	3.65	3.64	0.45
86B	CaO-MgO‡	......	2,000	4.17	4.18	4.18	3.73	3.74	3.74	0.44
88B	Limestone	10– 20	2,000	4.19	4.17	4.18	3.80	3.76	3.78	0.40
89B	Limestone	20– 40	2,000	4.19	4.17	4.18	3.78	3.74	3.76	0.42
90B	Limestone	40– 80	2,000	4.12	4.15	4.14	3.70	3.71	3.71	0.43
91B	Limestone	80–200	2,000	4.25	4.27	4.26	3.70	3.72	3.71	0.55
87B	Limestone	Comp.	2,000	4.18	4.20	4.19	3.72	3.76	3.74	0.45
93B	Dolomite	10– 20	2,000	4.21	4.24	4.23	3.75	3.79	3.77	0.46
94B	Dolomite	20– 40	2,000	4.12	4.08	4.10	3.72	3.74	3.73	0.37
95B	Dolomite	40– 80	2,000	4.07	4.09	4.08	3.68	3.72	3.70	0.38
96B	Dolomite	80–200	2,000	4.12	4.16	4.14	3.69	3.71	3.70	0.44
92B	Dolomite	Comp.	2,000	4.23	4.23	4.23	3.72	3.74	3.73	0.50
Average						4.16			3.72	0.44

* Average of 6 determinations.

† Burnt dolomite 46.53 per cent CaO and 32.85 per cent MgO.

‡ Mixture of separately calcined oxides.

pounds of CaO per 1,500,000 pounds of soil, or a percentage of 0.266. These earlier studies showed that all of the $Ca(OH)_2$ and $CaCO_3$ derived from the burnt lime, hydrated lime, or calcium carbonate had disappeared before the end of 10 days. In the present case, it follows, therefore, that any changes induced by the caustic forms for the 4-year period must have come from ab-

sorbed CaO, rather than from any appreciable residues of hydroxide or carbonate forms, except during the first 10-day period. Moreover, the imposition of intensive conditions in the laboratory failed to demonstrate any chemical disintegration of organic matter, so that all decreases found in the present study are considered as the result of biochemical accelerations.

Influence of surface-zone incorporations as measured by the surface-zone controls

It will be noted that the surface-zone of the control gave an organic CO_2 content of 4.19 per cent after 4 years, as compared with 4.12 per cent for a representative composite secured at the time the soil was placed in the tanks. Some oxidation of organic matter must have taken place in the upper zone. Such oxidation was probably at the minimum during the period when the direct rays of the sun were of maximum effect and when the upper surface was a dry crust too low in moisture for optimum bacterial activities. But, an actual *increase* in content over that of the original soil was found and must be accounted for. This may be due to two additive causes working jointly to offset and supplement the loss in original organic matter. The rainfall brings down a considerable amount of soot—as well as dust—which is retained upon, or near, the surface of the soil. No quantitative determinations of soot increment have been made, but observations necessitate consideration of this factor. Some organic matter may have been derived from algae and lichens, in spite of the effort to prevent all plant growth. Gravitational adjustment of soil particles in the unstirred leached soil may also have been a vitiating factor. The final composition of the untreated soil may be considered as having included these factors, as near as it was possible to control them. In the following comparison from the data of table 1, surface zone variations will therefore be dealt with primarily on the basis of the final composition of the upper-zone of the exposed controls, rather than that of the original soil.

Of the 16 treatments 15 caused results lower than the amount found in the exposed, but untreated, control. In the hydrated lime group the 2000-pound incorporation gave the lowest residual and greatest variation from the control. The 250-pound addition came next, with a difference hardly more than that to be permitted for experimental error, whereas the 500-pound and 1000-pound additions were practically identical, with some indication of decrease below the content of the exposed control.

The burned dolomite treatment was the one exception which showed no difference from the control, but the corresponding oxide mixture showed a considerable decrease, one somewhat greater than that found for the chemically equivalent hydrated lime treatment.

Each of the limestone separates and the composite showed a diminished organic matter content. The average reduction for the group was 0.16 per cent. The differences between the several limestone separates were small, however, and no definite influence of degree of fineness was registered. In

general the same obtains for the dolomite group, although the inactivity of the 10–20-mesh separate is definitely established as compared with that of the 80–200-mesh separate. The 5-unit average for limestone is practically identical with that for dolomite. There were found, therefore, no outstanding differences which could be attributed to variation in degree of fineness, nor to differential influences exerted by surface-zone incorporations of the two types of limestone.

Influence of surface-zone incorporations upon subsurface-zone changes

The data of table 1 also show that, for every treatment, the subsurface-zone content was less than that of its respective overlying treated zone, but the same variation was found also for the controls. The subsurface-zone of the exposed untreated tank shows an organic matter content 0.38 per cent less than that of its overlying zone and 0.31 per cent less than the original soil of initial uniform composition. This disparity was larger than that found in any of the 16 treatments, with one exception. As a whole the entire 16 treated tanks show a marked uniformity of lower-zone content and their average is identical with the residual content of the untreated control. It thus appeared that the amounts of alkali-earths which have passed from the upper zone and which have been fixed in the lower zone have not induced acceleration of biochemical processes in the lower zone.

The moisture content of the lower zone is nearly always greater than that of the upper-zone during the seasons when bacterial activities are most pronounced. Moreover, the lower-zone was never subject to the direct rays of the sun during the 4-year period. Brown (1) and King and Doryland (2) have shown that bacteria may be expected to be more abundant and physiologically more active in the second 4 inches of the surface soil. These factors are most probably responsible for the greater oxidation shown as a zone influence, without additive treatment.

Influence of subsurface-zone incorporations upon surface-zone changes

The data of table 2 show that in 4 of the 16 tanks, which received subsurface-zone treatment but no additions to the upper-zone, the organic matter content of the upper zone at the end of 4 years was slightly greater than that of the upper-zone of the exposed no-treatment tanks. However, 12 of the tanks showed a gain over the content of the original soil. In 5 of the 12 cases which showed an amount less than the exposed control, there was an analytical variation of only 0.01 per cent, whereas in the remaining 7 tanks the maximum disparity was 0.11 per cent. No definite variation therefore appeared to justify the assumption that underplaced caustic and carbonate treatments produced differential effects upon the overlying untreated zone. The average of the 3 fractional treatments of hydrated lime—250 pounds, 500 pounds, and 1000 pounds—the three 2000-pound caustic treatments, and the 10 limestone and

dolomite treatments shows a 4.16 per cent content against 4.19 per cent for the soil which received no treatment in either zone. It is thus apparent that no ultimate decrease in organic CO_2 was produced in the upper zone as a result of the lower-zone incorporations.

Influence of subsurface-zone incorporations as measured by the subsurface-zone controls

The final organic matter content of the lower zone of the control was identical with that of each of the tanks which received lower-zone incorporations of hydrated lime at the 250-pound rate and limestone and dolomite of 10–20-mesh fineness. The 500-pound and 1000-pound rates of hydrated lime showed an identical disparity of only 0.07 per cent, whereas the maximum minus variation induced by any one of the 8 limestone and dolomite separates and by the CaO-MgO mixture was 0.08 per cent. The burned dolomite and CaO-MgO mixture registered 0.14 per cent and 0.04 per cent, respectively, less than the control, whereas the maximum decrease of 0.22 came from a chemically equivalent addition of hydrated lime. It has been pointed out that this hydrated lime incorporation was fixed by the soil in less than 10 days, and that only the finer limestone separates had been completely disintegrated (4) after 4 years, so that the somewhat greater decomposition must be attributed to initial influences resultant from greater availability and more rapid assimilation. In other words, practically the full amount of the hydrated lime incorporation was quickly "fixed" (5) and effective throughout the entire 4-year period, whereas the limestone incorporations were not; varying fractions of the several limestone incorporations were, in a sense, inert during their persistence as undistintegrated particles. The average of all 16 additions, 13 of which were at the same rate, amounted to 3.72 per cent, as compared to 3.78 per cent where no addition was made to either zone.

Comparison of all surface-zone units, with and without incorporations

In table 1 the changes induced by the 16 surface-zone incorporations are given, whereas table 2 gives the same number of units which were subject to no alkali-earth increments, except any which might have moved upward from the lower zone of incorporation. It has been shown that surface-zone additions induced no decrease in subsurface-zone organic matter and that subsurface-zone incorporations failed to decrease the organic matter content of the untreated upper zone. Comparisons may therefore be made between the 16-unit series to which additions were made in the upper zone and the corresponding series where no surface-zone incorporations were made. These respective comparisons are given in condensed form for the 2000-pound CaO-equivalent incorporations in figure 1. The more extensively decomposed and "fixed" (5) 80–200-mesh limestone and dolomite separates are utilized. In the case of the no-treatment surface group, 87B-91B, the closely agreeing units were

averaged. When the results from the surface-zone, to which the different additions were made, are compared with the results from the same zone without additions, some stimulation in oxidation of soil organic matter was registered by 14 of the 16 treatments, if it may be assumed that the same increment of organic matter came to each tank from rainfall and restricted growth of the lower forms of plant life. The reverse obtained, though to an extent of only 0.05 per cent, for the 1000-pound CaO-equivalence of hydrated lime and also, to the extent of 0.11 per cent, for the burnt dolomite addition. As an average of all fractional and full treatments, the alkali-earth additions gave organic CO_2 residuals 0.13 per cent less than the average given by the 16 tanks where the surface-zone was untreated. The thirteen 2000-pound surface-zone incorporations gave fairly uniform residuals. The same holds for the 13 corresponding tanks where no incorporations were made in the upper-zone. If the difference found between their respective averages of 4.03 per cent and 4.16 per cent shows an actual loss of 0.13 per cent for the 4-year period, or an annual loss of 0.0325 per cent, such a small loss would probably be offset by organic matter derived from crop residues.

Comparison of all subsurface-zone units, with and without incorporations

The foregoing basis of comparison may also be applied to the lower zone. Each addition gave an apparent enhancement in oxidation of the lower-zone organic matter. In some cases the enhancement is relatively small. The minimum for the limestone series was 0.04 per cent and the maximum 0.11 per cent for the composite and 40–80-mesh product, respectively. Corresponding extremes of 0.01 per cent and 0.15 per cent obtained for the 10–20-mesh and 40–80-mesh separates of dolomite. No positive relation between rate of treatment and increase in oxidation showed for the 250-, 500-, and 1000-pound CaO additions, whereas the two CaO-MgO supplements were practically identical. The greatest enhancement of all came from the 2000-pound CaO-equivalent incorporation of hydrated lime, where the increased oxidation in the lower-zone over that of the upper-zone amounted to 0.30 per cent. This represents practically the same effect as that registered by the hydrated lime in the upper zone. The grand average of the 16 subsurface-zone residues, where no additions were made to the lower zone, was 3.81 per cent against 3.72 per cent as a corresponding average from the 16 subsurface-zone incorporations, i.e., an average increase of 0.09 per cent in oxidation as a result of additions. A similar comparison of averages for the thirteen 2000-pound incorporations gives an increase of 0.10 per cent attributable to the average accelerative effect from the subsurface-zone incorporations.

Zone effect versus influence of additions

From the comparison of surface-zone incorporations with the untreated exposed control, it appeared that 15 of the 16 treatments caused some enhance-

ment in oxidation of organic matter; but from an inter-zone comparison for each of these tanks, it developed that the subsurface-zone conditions minus additions were more conducive to oxidation than were the surface conditions plus treatment. The average for the subsurface-zone-condition effect without incorporations over that of the surface-zone effect plus treatments amounted to 0.24 per cent. This constitutes an absolute zone-basis loss of 2400 pounds or 4800 pounds upon the full 2,000,000-pound basis. It has been pointed out that this greater loss in the lower zone is not to be attributed to any acceleration induced by influx of alkali-earths from the several treatments in the upper zone, since the disparity between the final contents of the two zones in the two untreated exposed controls was greater than analogous disparities in 15 of the 16 incorporations.

From the data of table 2 it appears that the combined factors of alkali-earth treatment and more favorable conditions for bacterial activities in the lower-zone were responsible for an average disparity of 0.44 per cent in comparison with the average of all exposed no-treatment upper-zone units. This disparity, however, represents the differential from a grand no-treatment surface-zone average which showed very little deviation from the organic-CO_2 content of the exposed control. In the several individual disparities used to obtain this average, each minus variation was larger than its corresponding one in table 1. It has been pointed out that for any oxidation which occurred in the surface zone there was an apparent offset from organic matter increments, or gravitational adjustment.

The maximum differentials between subsurface-zone and surface-zone activities came from the 2000-pound hydrated lime treatment and from the 80–200-mesh limestone separate. The other treatments do not show sufficiently great nor consistent differences to warrant special stress.

The average effect of the thirteen 2000-pound surface-zone incorporations was to produce an oxidation 0.14 per cent in excess of that which took place in the untreated soil, so that the full average oxidative increase exerted in the lower zone, per se and minus contact treatments, was therefore found to be 0.38 by the two calculations $4.19 - 4.05 + 0.24 = 0.38$ and $4.19 - 3.81 = 0.38$. Similar calculations of $4.19 - 4.16 + 0.44 = 0.47$ per cent and $4.19 - 3.72 = 0.47$, give the greater average oxidation exerted by the lower zone plus contact treatments. An average value of 0.09 per cent is thus obtained as representing the accelerative oxidation exerted by a 2000-pound CaO-equivalent during the 4-year period. Again, from the 4.03 per cent average for the thirteen 2000-pound CaO-equivalent incorporations in the surface-zone and the corresponding 4.16 per cent surface-zone average in the series which contained no surface-zone incorporations, it appears that the lime incorporations produced an average organic CO_2 decrease of 0.13 per cent in the surface zone during the 4-year period. As a general conclusion, it may be said that an average annual decrease of from 0.025 to 0.03 per cent organic CO_2 occurred as a result of the lime additions, irrespective of zone of incorpora-

tion. This may be considered as fairly representative of the value of all 2000-pound incorporations, with the exception of the hydrated lime to which a higher value should be given.

As a salient point, it may be stressed that the zone influence effect upon biological conditions appears to have been a more potent factor than ameliorents, for this particular soil.

SUMMARY

Determinations of organic matter changes in surface-zone and subsurface-zone samples from 34 lysimeters are given to show the influence of surface-zone and subsurface-zone incorporations of 2000-pound and fractional incorporations of hydrated lime and 2000-pound CaO-equivalences of burnt dolomite, separately calcined mixtures of CaO and MgO, 4 separates and their equal-part composite of limestone and of dolomite after a period of 4 years' exposure without crops and without stirring.

The final organic CO_2 content of the surface-zone of the untreated exposed soil was somewhat greater than that of the original soil, whereas the subsurface-zone content was decidedly less. This offset to surface-zone oxidation was attributed to the combined agencies of soot depositions, and algae and similar growth upon the upper crust and to possible gravitational readjustment of soil particles. The marked loss was attributed to greater bacterial activities induced by the more moist conditions of the lower zone, during the period of maximum bacterial activity, and by the absence of any direct sunlight.

Of the 16 surface-zone incorporations, 15 showed oxidation of organic matter, on the basis of the content of the exposed untreated control. The decreases induced by the 4 rates of hydrated lime were not extensive, nor in proportion to the rate, although the maximum rate gave the maximum decrease.

No positive differences in organic-CO_2 residues were found to be attributable to variation in fineness of limestone in the surface-zone, and although some variation was noted between the coarsest and finest of the dolomite separates, the group averages for the two limestones were identical.

All untreated subsurface-zones were found to be of lower organic matter content than their corresponding overlying treated zones, although in 15 of the 16 treatments the differences were less than the zone variation found in the controls. This uniformity in lower-zone composition shows that no appreciable activation was induced by calcium-magnesium leachings from the incorporations made to the upper zone.

No evidence was adduced to show that subsurface-zone incorporations had any accelerative effect upon oxidation of surface-zone organic matter.

With the exception of two of the 2000-pound caustic additions, no marked variation from the control was obtained, nor was any influence of fineness shown for lower-zone incorporations.

Of the 16 surface-zone incorporations, 14 gave organic matter residues which

were less than their respective surface-zone analogues in which no incorporations were made.

Each of 15 of the 16 subsurface-zone incorporations resulted in a decrease in organic matter beyond that of its corresponding subsurface-zone where no incorporation was made, the maximum variations having been produced by the 2000-pound rate of hydrated lime and its equivalent of 80–200-mesh limestone.

In general, the accelerative effects of the liming materials were comparable in the two zones.

The zone-influence appeared to be more potent than that of alkali-earth incorporations in producing oxidation of the organic matter of this particular soil under fallow conditions without stirring and with only natural rain water.

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THE PHENOMENA OF CONTRACTION AND EXPANSION OF SOILS WHEN WETTED WITH WATER

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Soil colloids swell when they take up water. The question is, however, does the total or absolute volume of the colloids and water considered together, increase or decrease when the dry colloids are brought in contact with water. If the absolute volume increases, it indicates that the swelling is greater than the volume of water taken up in the process; if the absolute volume decreases, it indicates that some of the water adsorbed in the swelling process has been compressed; if, on the other hand, the absolute volume remains unchanged, it would logically seem that the swelling of the colloids is equal to the volume of water taken up, and that the colloid has not expanded additionally, nor has the water contracted or been compressed. It is the object of this paper to present experimental data bearing upon these points.

PROCEDURE AND METHODS

Three different and distinct methods were tried in measuring the volume changes that take place when dry soils or colloids, are brought into contact with water. The first method consisted of rolling puddled soil into certain size pellets, drying them, then dipping them a few times in gelatine solution until a good coating of gelatine was formed around their surface and drying them again either in room temperature or in an oven at 110°C. temperature. These pellets were then dropped into a dilatometer containing water, which was maintained at a definite temperature in a bath, usually at 20°C. This dilatometer was quickly stoppered and placed back in the constant temperature bath and the readings on the dilatometer stem were taken regularly until they became constant, which indicates that the dilatometer contents have attained the temperature of the bath. Inasmuch as the dry gelatine does not dissolve at 20°C. and the water could not penetrate it in the short time required for the attainment of equilibrium, the soil in these pellets remained dry. In order that the soil might come in contact with the water, the dilatometer with its contents was placed in a water bath having a temperature of about 35°C., and kept there for a few minutes until the gelatine coating began to dissolve and the water to penetrate the soil. The dilatometer was then brought back to the original temperature, allowed to attain equilibrium with the original temperature, and the readings were taken again. With the knowledge of the

readings before the dilatometer was placed at the higher temperature bath and after it was brought back to the original temperature bath and equilibrium attained, any differences could be easily ascertained. Inasmuch as the gelatine

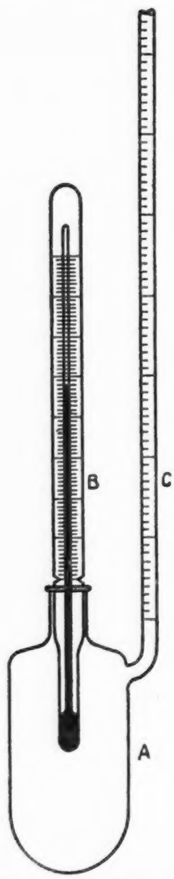

FIG. 1. DILATOMETER FOR MEASURING VOLUME CONTRACTION OF SOILS WHEN WETTED WITH WATER

also takes up water, allowance for this error was made in the final calculations of the results.

The second method consisted of placing a certain quantity of dry soil in a dilatometer, covering it with a layer of dry mercury, then filling the remainder of the dilatometer with water and stoppering it. The mercury being heavier than water, prevented the water from coming in contact with the soil until the

desired time. This dilatometer was then placed in a constant temperature bath until equilibrium was reached, and the reading on the stem was recorded. Then the dilatometer was tilted, allowing the water to come in contact with the soil. After the soil was thoroughly wetted, the apparatus was allowed again to come to equilibrium in the constant temperature bath and the final reading again recorded. Provided no errors entered in the experiment, any differences in the two readings should show contraction or expansion in the absolute volume, due to wetting of the soil colloids with water.

Although both of the foregoing methods gave results which were interesting and significant and indicated that a change did take place in the volume when soils and water were brought in contact with each other, yet these results did not possess as great accuracy as was desired. One of the features which seemed to introduce a considerable error in the results was the air contained in the soil. On account of its compressability and certain other properties, the air enclosed either in the pellets or under the mercury layer seemed to introduce a definite and variable error.

To overcome this difficulty, it was decided to devise a new method, wherein the factor of soil air was entirely eliminated. Accordingly, the next or third method that was employed consisted of placing a definite quantity of soil in the dilatometer, drying it in an oven at 110°C. for 24 hours, then quickly but gently pouring into the dilatometer sufficient carbon tetrachloride to cover the soil. Then with a glass rod the soil mass was stirred and the air was all displaced by the organic liquid. The dilatometer was then filled with water, stoppered, and placed in a constant temperature bath, and after equilibrium was attained, it was tilted allowing the water and the soil to come into intimate contact. The readings before and after the soil and water were mixed showed the differences, if any, that occurred in the volume.

This method worked remarkably well. As carbon tetrachloride is heavier than water, the latter could be prevented from coming into contact with the soil before the desired time; carbon tetrachloride penetrates the soil mass sufficiently to displace completely all the air present, and the water in turn displaces this carbon tetrachloride so that the reaction taking place between the soil and the water is the same as though the soil were never treated with carbon tetrachloride or as if this liquid were not present. In view of all these facts, the method is exceedingly accurate, simple, and practical, and is probably most exceptional for investigations of the type herein described.

It might be argued that if the carbon tetrachloride wets the soil so as to displace the air from its pores and from around its particles, the water probably cannot wet the soil completely and consequently probably there cannot be the same kind of reaction as if the organic liquid were not present. However, experiments conducted during this investigation as well as those reported in previous publications (1) show that the presence of the carbon tetrachloride has absolutely no adverse effect on the reaction between the soil and water, especially in the case of the mineral soils. For instance, if water is added to

soils, except muck and peats, in the dry condition, while they are immersed in carbon tetrachloride or ligroin, the amount of heat evolved is practically the same as in water alone. This most interesting and significant fact indicates that the specific attraction of the solid materials for water is not destroyed by the presence of carbon tetrachloride or ligroin; and that this attraction will penetrate a solid film of carbon tetrachloride or ligroin to reach the water and

TABLE 1

Relationship between volume of contraction when soils are wetted with water and their respective colloidal content and heat of wetting values

SOIL	VOLUME OF CONTRACTION PER 100 GM.	COLLOIDAL CONTENT	HEAT OF WETTING PER GRAM	COLLOIDAL / VOLUME OF CONTRACTION	HEAT / VOLUME OF CONTRACTION
	cc.	*per cent*	*calories*		
Sand	0.033	1	0.350	30.30	5.30
Fresno Sand Loam	0.216	18.00	1.120	83.30	5.18
Hillsdale Sand Loam A_2	0.206	15.73	0.930	76.35	4.51
Hillsdale Sand Loam B_1	0.240	18.70	1.190	77.50	4.95
Hillsdale Sand Loam B_2	0.233	20.42	1.240	87.60	5.32
Napanee Silt Loam A_1	0.550	35.57	1.960	64.67	3.56
Napanee Silt Loam C	0.337	50.76	1.990	150.60	5.90
Mich. Silt Loam	0.593	39.04	3.600	65.80	6.58
Ohio Silt Loam	0.433	35.00	2.109	80.80	4.87
Tenn. Silt Loam	0.616	32.41	2.450	52.61	3.97
Minn. Carrington Silt Loam	2.533	56.44	9.340	22.28	3.69
Ill. Bloomington Clay Loam	1.633	40.00	4.460	24.49	2.73
Ill. Urbana Clay Loam	1.570	41.95	3.640	26.71	2.31
Calif. Yolo Loam	1.066	48.49	4.490	45.48	4.21
Calif. Yolo Clay Loam	1.350	59.54	5.930	44.10	4.39
Calif. Yolo Clay	1.330	58.34	6.430	43.89	4.83
Ontonagon Silt Loam A_1	0.850	60.65	3.940	71.35	4.63
Ontonagon Silt Loam A_2	0.940	57.60	4.230	61.27	4.50
Ontonagon Clay B_1	0.9033	70.00	6.600	77.49	7.30
Colloids from Ontonagon Silt Loam A_1	1.733	100.00	9.600	57.70	5.53
Colloids from Ontonagon Silt Loam A_2	1.430	100.00	9.660	69.93	6.75
Colloids from Ontonagon Clay B_1	1.533	100.00	10.420	65.23	6.79
Muck	4.666		30.100		6.45
Silica Gel	1.620		24.500		
Fullers earth	4.266		16.000		
Ontonagon Clay B_1 (moist)	0	70.0			

thus satisfy itself. The distance to which this force will be felt, even through an intervening solid film of another liquid, is considerable.

Hence any objection that might be raised against the use of carbon tetrachloride in the present experiments seem to be set aside by actual tests.

The dilatometer apparatus used is shown in figure 1. It consists of two parts, the bulb and the stem. The bulb has a capacity of 100 cc. The stem

is a 2-cc. pipette which is calibrated to 0.01 cc. and the readings can be estimated to a smaller value than that. The mouth of the bulb was stoppered with cork or rubber, both of which proved satisfactory.

EXPERIMENTAL DATA

In table 1 are presented the experimental data obtained on the volume changes when soils dried at 110°C. for 24 hours, are brought in contact with water, by the third method. The amount of soil used in all cases, was 30 gm., calculated on the absolute dry basis. The figures presented herewith, however, are calculated on the basis of 100 gm. of soil. The figures show the amount of contraction, in cubic centimeter that the original volume underwent, when the water and the soil were brought into intimate contact, or when the soil was perfectly wetted and saturated with water.

An examination of the data in the above table reveals immediately many most interesting and significant facts. In the first place it shows that when oven-dry soils are wetted with water a contraction takes place. The volume of this contraction varies markedly with the different soils—0.033 cc. per 100 gm. of soil in the case of sand, 0.616 cc. in Tennessee silt loam, 1.350 cc. in Yolo clay loam, 2.533 cc. in Carrington silt loam, and 4.666 cc. in muck. Apparently, the soils that tend to give the smallest value of contraction are the light soils, especially the sand; and the soils that tend to give the highest value of contraction are the heavier or colloidal types of soil and the organic soils. Of all the materials used, muck gave the highest value, with Fullers earth coming next in order. From the results with muck, it would be logical to conclude that soils containing considerable amounts of organic matter would yield a correspondingly larger value of contraction, and such appears to be the case as evidenced by the results with Minnesota Carrington silt loam, and with Illinois Bloomington clay loam. The interesting thing to be noticed is that mineral soils with organic matter give as great or greater values of contraction as pure colloids extracted from mineral soils. For instance, the colloids extracted from the A_1, A_2, and B_1 horizons of the Ontonagon soil, which is classed as silt loam in the first two horizons and as clay in the last, do not show any greater volume of contraction than do some of the soils containing various amounts of organic matter. On the other hand, the colloids gave almost twice as great volume of contraction as the corresponding soils from which they were extracted. In this connection it is of much interest to ascertain what relationship there really is between the volume of contraction, colloidal content, and heat of wetting of the different materials used. This relationship is represented in table 1, which contains the values for contraction colloidal content as determined by the heat of wetting method, and by the heat of wetting values.

By comparing first the colloidal content with the volume contraction in table 1 it is seen that there is a general relationship, but not always a very close one, between them. There is a general tendency for soils with the largest amount of colloidal material to give the greatest amount of volume contraction,

but there are some exceptions. For instance, the A_1 horizon of Napanee silt loam has 35.51 per cent of colloidal material and shows a volume contraction of 0.550 cc., whereas the C horizon of the same soil has 50.76 per cent of colloidal material and shows only 0.337 cc. of volume contraction. There is, of course, a reason for this discrepancy. The C horizon contains a very high content of carbonates and has not undergone the extreme weathering process that the above horizons have. Furthermore, the A_1 horizon of this soil contains some organic matter which tends to destroy any close relationship. Possibly the two factors that tend to prevent a very close relationship between the volume of contraction and colloidal content, are differences in organic matter content and in activity or state of hydration of the materials.

By considering next the volume contraction with the heat of wetting, it will be readily seen that there is a rather close relationship between them. Indeed, the ratio ranges from 2.31 to 7.30 between the mineral soils and from 2.31 to 6.45 between the lowest value in the mineral soils and muck. Apparently, this is a little closer relationship than that between the volume contraction and the colloidal content.

The question now is, what causes the contraction in volume when absolutely dry soils are wetted with water.

A comprehensive consideration indicates that the volume contraction in the case of the soils, is due to two chief factors (*a*) chemical hydration of water and (*b*) physical compression of water. Of the two, the last is probably of the greatest importance. In both cases, however, there is a condensation of water and consequently a decrease in the original volume.

One of the strongest evidences that the volume contraction is due to the above factors, is the heat evolved when dry soils are wetted with water. The evolution of heat of wetting represents an expenditure of energy on either one or both of the reacting materials. Since the soil colloids, which are mainly responsible for the heat of wetting, are comparatively insoluble, practically the entire expenditure of energy must be at the expense of the water alone. This expenditure of energy on the part of the water also represents a transformation in its state of aggregation, probably from the liquid to the solid or semi-solid phase. In the case of solid materials, such as soil colloids, which adsorb water as film on their surface, the film must be under great compression, and probably approaches the solid state of aggregation. The force with which the effective water film is adsorbed and probably compressed, amounts to more than 150,000 atmospheres per 100 gm. of soil, as shown in previous investigations (2). This water thus compressed must be represented, therefore, in the volume contraction under consideration.

But how is the general notion explained that soil colloids swell when they take up water, if there is an actual decrease in the original total volume? The general notion takes into consideration the volume of the soil alone and not that of the total volume of the soil and water together. It is true that the apparent volume of soil colloids increases when they absorb water, but this

increase or expansion is due to the water they take up or imbibe. The greater the amount of water the material will imbibe, the greater its expansion should be. In this connection it is interesting to observe that of all bhe soil constituents, the organic matter undergoes the greatest swelling when it takes up water. Yet it has been seen in the present investigation that muck and soils containing organic matter caused the greatest amount of contraction of the absolute original volume. It would appear very suggestive, therefore, that there might be a connection between the amount of water that is compressed and the apparent swelling of the material.

A few observations made during the course of the investigation might be mentioned here. If the soil contained its normal volume of air, there would always be an increase instead of a decrease in the volume when the soil was wetted with water. The increase in volume would vary with the amount of air present. When the air, however, was displaced, as was done by carbon tetrachloride, then the volume always decreased and the results could be repeated almost exactly. Another fact observed was that when the soils were brought into contact with water after being immersed under the column of carbon tetrachloride, the mineral soils would wet with water almost instantaneously, but the mucks, peats, and soils containing high organic matter would wet very slowly—a complete wetting would finally take place, such as in the mineral soils, but it would take longer. The length of time, however, was considerably shortened by shaking the contents.

SUMMARY

An investigation was conducted to ascertain the volume changes that take place when absolutely dry soils are wetted with water.

A specially constructed dilatometer was employed for measuring these volume changes.

It was found that when absolutely dry soils are wetted with water, the original volume of the soil and water is decreased. This volume contraction varies with the different soils. The organic matter constituent tended to give the greatest volume contraction.

An examination was made to ascertain what relationship this volume contraction has to the colloidal content, to the organic matter content, and to the heat of wetting phenomenon. The results showed that the volume contraction has a very close relationship to the organic matter content and to the heat of wetting phenomenon. It also has a relationship to the colloidal content, but this is not so consistent and so close as in the other two cases.

Although soil colloids expand when they take up water, the total volume of the colloids and water considered together, undergoes a contraction.

This contraction in the volume is attributed principally to the condensation of some of the water on the surface of the soil particles or colloids. A small portion may also be due to hydration.

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COLLOIDAL BEHAVIOR OF SOILS AND SOIL FERTILITY: III. CATION REPLACEMENT AND SATURATION OF SOIL WITH Ca[1]

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The response of some soils to lime has been known and liming for soil improvement has been practiced for a long time. Although the Ca ion is one of the essential plant constituents, lime has not been applied as its source. Until quite recently the sole object in liming soils has been to neutralize the acids in the soils; the real function of lime, notwithstanding the voluminous researches, has long remained obscure. Only after the factors involved in the process of base exchange were determined and after the lime problem was attacked from the physico-chemical standpoint has the solution heen approached.

It has been pointed out (5) that, from the standpoint of crop producing power, soil constituents may be grouped into two broad divisions: active and passive. The passive consists of that portion of the soil which is practically inert as far as the immediate fertility of the soil is concerned: it serves the purpose of mechanical support. In the process of weathering, some of the representative classes of this passive division, like the feldspars, slowly disintegrate from the surface. The disintegration products replenish the active division in which the life of the soil is concentrated. It is this active division that comprises what is known as the soil "complex capable of base exchange." The hydrated aluminum silicates with replaceable Ca, Na, K, and sometimes Mg and H are representatives of this complex. To this portion belongs also that class of humus compounds which are capable of forming complex humates of Ca, Mg, Na, K, or H. It is within this division of the soil make-up that most of the reactions in relation to release and retention of plant-food take place. This active portion is chiefly of colloidal nature and is therefore sometimes referred to as the "colloidal fraction" of the soil.

Capacity for base exchange is an inherent property of every soil and is practically constant unless the soil undergoes drastic treatments that cause deterioration, as shown below. Whenever a soil undergoes cropping, with or without fertilization, the qualitative relationships, but not the capacity, of the various cations in the soil complex capable of exchange varies. If hydrogen ions predominate in the complex, the soil becomes unsaturated and

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acidity appears. This condition is accompanied by a diminution of the other cations, such as Ca, Mg, K, and Na, which are forced out by the H ions (5).

The acid reaction is thus responsible not only for the acid condition per se, which in turn results in solubilizing the harmful Fe and Al ions, but also for depleting the soil of its valuable bases essential for plant growth. It is also important to remember that a complete unsaturation is inducive to a loss of the complex capable of base exchange, both mineral and organic. It has been pointed out (5) that the so-called zeolites with hydrogen as the only cation are more soluble than those with bivalent cations, or with a combination of mono- and bivalent cations, and under certain conditions may be leached out. The same thing occurs with the humates when their cations are replaced with hydrogen.

In order to determine the capacity of any soil for base exchange, 10-gm. samples are treated with 250 cc. of neutral *N* NH_4Cl, left in contact with it for 6 days, and filtered. The soil on the filter is then washed with fresh portions of NH_4Cl solution until the filtrate gives no trace of Ca and maintains the reaction of the neutral NH_4Cl. From 4 to 6 liters of solution are necessary (depending on the base exchange capacity) to complete the replacement. The soil is then washed with distilled water until free from chlorides, and the ammonia determined by distillation.

The NH_4 content may be checked in the following way: the same soil is saturated with the K ion, neutral *N* KCl solution being used. The total *N* is then determined on both the K- and NH_4- saturated soils. The difference in *N* content in terms of NH_4 may be taken as the amount of *N* absorbed by the complex, The latter method, which was checked repeatedly by determining the NH_4 present in the original soil before treating with NH_4Cl, was found to be very satisfactory.

A number of soil samples of the Chenango series was treated with normal NH_4Cl solution and the ammonia absorbed, after replacing all other cations, was determined as described. Simultaneously the H ions present were determined and checked by treating the soils with *N* $BaCl_2$ solution and titrating the extracts and leachings with 0.02 *N* KOH to pH 6.8 to 7.0.

The results are summarized in table 1.

In general the data show that the heavier types of soil have a greater base exchange capacity than the lighter types. This, of course, is to be expected, since the heavier soils contain a large amount of the so-called colloid fraction which is chiefly responsible for the replacement reactions. This phase will be discussed fully later when the results of the experiments on the base exchange capacity of the soils from the soil fertility plots are reported. For the present an analysis of the data will be made from the standpoint of saturating the respective soils with Ca.

Let us for a moment picture in general the possible effects of adding lime to a soil depleted of its bases to various degrees through the accumulation of H ions.

The Ca ions will enter the soil complex capable of base exchange, forcing out the H and any other cations present. The Ca ions from the other calcium compounds present in the soil together with the ions going in and out from the complex possess various properties.

First, Ca is an essential element; secondly, the Ca ion is an antagonist performing an important function in balancing the physiological equilibrium of salt intake by plants, as has been shown by the researches of Osterhout (9), Loeb (8), Lipman (6), and many others; thirdly, Ca affects the degree of dispersion of the soil colloids. The divalent character of the Ca ions is of great moment in determining the degree of dispersion of the soil particles, which affect in a large measure the soil structure, increasing porosity and producing a granular structure. The sum total of the effect of the Ca ion on the colloidal reactions of the soil may be expressed by the suction force of the soil, as has been shown (5). It is also easily demonstrable by a determination of the heat of wetting method of Bouyoucos (2) and Anderson (1) as was shown by Parker.[2]

TABLE 1

Degree of unsaturation of soils, Chenango series

SOIL NUMBER	TYPE OF SOIL DESIGNATED BY SOIL SURVEY	REACTION OF H_2O EXTRACT	NH_4 ABSORBED PER 100 GM. AIR-DRY SOIL	REPLACEABLE H IONS IN 100 GM. SOIL IN TERMS OF NH_4	UNSATURATION
		pH	*mgm.*	*mgm.*	*per cent*
1	Loam	5.0	64.69	36.44	56.30
2	Loam subsoil	5.0	97.49	54.49	55.89
3	Silt loam	5.0	82.91	42.00	50.70
4	Silt loam subsoil	5.0	67.42	31.28	46.30
5	Sandy loam	5.0	51.02	32.18	63.08
6	Sandy loam subsoil	5.6	55.58	6.91	12.43
7	Fine sandy loam	5.8	64.69	14.00	21.64
8	Fine sandy loam subsoil	6.0	31.89	7.65	23.98
9	Fine sand	5.2	37.36	13.45	36.02
10	Fine sandy subsoil	5.2	51.93	14.72	28.35
11	Sand	4.6	35.53	20.74	58.30
12	Sandy subsoil	5.0	26.42	4.72	17.89

A consideration of the effect of Ca on the acid reaction of the soil solution—the elimination of the obnoxious Fe and Al ions on one hand and the locking up of phosphates and Fe on the other—is important. A good deal of work on this phase of the problem has been carried out by the authors and will be reported in a forthcoming paper of this series.

Last comes the effect of the Ca on certain biological activities in the soil,

[2] Paper read before the symposium on base exchange at the Chicago meeting of the American Society of Agronomy, November, 1925.

which determine the organic matter content and differentiate the relative quantities of the various fractions of organic matter, as was shown by Tyulin (10).

Table 1 shows that the total capacity of the soils for base exchange cannot be taken as a criterion for the saturation of the soil with Ca. If such a procedure should be followed it would mean that the soil would contain no cations for replacement except Ca. The deleterious effects of such a condition would be comparable to overliming, as any phosphorus fertilizers would immediately become precipitated; potassium fertilizers would be more easily leached out because the energy of replacement and adsorption of the Ca ions is greater than that of K ions.

The only logical method of applying lime is to introduce enough, in milligrams equivalent, of the H ions found by replacement and titration, to saturate the complex. Table 1 shows that each soil has a different value of base exchange capacity, with a different amount of H ions present. Each soil differs from its subsurface soil in acidity, and in general the subsurface soil is less acid, except in soils 1 and 2. The high colloid content of these soils, especially of the subsurface soils, tends to obliterate the differences.

Of course the colloid fraction is smaller in the sandy soil, and its subsurface soil has had no chance to receive basic cations from the topsoil; therefore, the podsolization in the soil profile has reached a lower horizon than in the clay soils.

In the loam soil the H ions are larger in absolute figures in the subsurface soil than in the topsoil; but relatively they are not, since the capacity for base exchange in the subsurface soil is practically one-third higher, as may be inferred from the figures on NH_4 absorbed.

The total replaceable hydrogen in the soils with a high colloid fraction increases with the degree of unsaturation. It may readily be seen that soil 5 with a pH of 5.0 will require fewer Ca ions to satisfy its unsaturated condition than soil 3; the saturation capacity for lime depends in a great measure on the base exchange capacity and on the degree of unsaturation. The only rational method of liming is, therefore, to introduce enough Ca ions to take care of the H ions present in replaceable form, and also of the hydrolytic acidity due to some of the Al and Fe compounds found in some soils.

At this point it is worth while to emphasize again the fallacy of pH readings as a criterion for measuring soil acidity. There is no correlation between the pH and the total replaceable H ions in the soil complex.

The degree of saturation or unsaturation of the top and subsurface soil gives a picture of the process of podsolization and the fate of the cations replaced.

In general the process goes on as follows: the ratio of the cations of the topsoil, where the bulk of the chemical and biological reactions takes place, is constantly changing depending on the factors of climate, tillage, and cropping. Certain cations enter the soil solution and are taken up by the plant,

others leave the soil solution to enter the complex capable of base exchange. On account of their high coefficient of replacement, the H ions from the organic acids in the process of organic matter decomposition, and inorganic acids produced by chemical interaction of the inorganic constituents with the organic acids, force out the basic cations; this action depletes the topsoil bases.

As mentioned, some of them are taken up by the plant, some are moving downward with the water and are caught by the subsurface soil, some enter the underground waters and are carried into the streams. It is easy to see that the

TABLE 2

Comparison of the lime requirement according to theVeitch method and H ion replacement with N $BaCl_2$; plot soils

LABORATORY NUMBER	PLOT NUMBER*	REACTION OF WATER EXTRACT	REACTION OF N $BaCl_2$ SOLUTION EXTRACT	LIME REQUIREMENT (CaO) PER ACRE		
				Veitch method	H ion replacement method with†	
					N KCl solution	N $BaCl_2$ solution
	1914	*pH*	*pH*	*pounds*	*pounds*	*pounds*
1	7A	5.6	4.8		1073	1156
2	10A	5.4	4.8		1042	1010
3	11A	5.4	4.4		1844	1802
4	12A	5.6	4.8		1020	1021
	1918					
5	7A	5.4	4.8	1000	1396	1349
6	10A	5.6	5.0	1000	1082	1042
7	11A	5.0	4.4	2000	1926	1802
8	12A	5.6	5.1	1000	844	844
	1922					
9	7A	5.2	4.6	1000	1365	1365
10	10A	5.4	5.0	1000	1140	1072
11	11A	5.0	4.4	2400	2312	2200
12	12A	5.6	5.0	1000	936	880

* 7A is the control—no fertilizers; 10A received $Ca(NO_3)_2$ equivalent in terms of N to 320 pounds of $NaNO_3$ per acre; 11A received $(NH_4)_2SO_4$, equivalent to 320 pounds of $NaNO_3$; 12A received $CaCN_2$, equivalent to 320 pounds of $NaNO_3$; all plots, eccept 7A, received yearly besides the nitrogenous fertilizers also 400 pounds of 16 per cent acid phosphate and 200 pounds of muriate.

† This includes the lime necessary to neutralize the acidity due to hydrolysis of Al compounds present.

monovalent cations are more quickly lost, because they do not possess so high a coefficient of replacement and absorption as the bivalent cations.

It will be recalled that the descending order of the energy of replacement and absorption of cations is: Ca, Mg, K, NH_4, and Na, and for this reason Na goes out first.

Theoretically, therefore, the unsaturated surface soils could be greatly improved by subsoiling wherever the subsurface soil retained the leached bases. The unsaturated soils would then become the portion that would retain the

leached out bases which would replace the H ion of the underplowed unsaturated portion.

The part of the underplowed unsaturated topsoil (now subsurface soil) receiving the bulk of the replaced cations from the surface soil, which was previously a subsurface soil saturated with bases, will retain some of the cations, especially the bivalent cations, and become saturated. Thus, subsoiling an unsaturated soil would afford a means of maintaining its fertility, since the valuable basic cations would be retained in the plowed horizon and would circulate there.

Samples 5 and 6 are very striking illustrations. The topsoil has become unsaturated, whereas the subsurface soil, which has a capacity for base exchange close to that of the topsoil, has retained almost all of its bases. Such a soil is on the verge of losing its bases also from the subsurface soil. Subsoiling would bring into the plowed horizon a complex with a high capacity of valuable cations which may be utilized by the plants. The practical aspect of this problem is now under consideration and as soon as results accumulate they will be published.

From what has been said it may be inferred that the so-called "lime requirement" is linked up with the determination of the state of unsaturation. It will be of interest, therefore, to compare a few figures of the lime requirements as determined by some of the standard methods and by the replacement method.

Table 2 gives the data on the lime requirements of soils from a few of the soil fertility plots at the New Jersey Experiment Station. The data for the lime requirements [Veitch method (11)] were taken from the files of the Soil Fertility Department.[3]

The lime requirement by the replacement method was determined as follows:

Ten-gram samples of the respective soils (sieved through a 2-mm. sieve) were treated with 250 cc. of *N* $BaCl_2$ or *N* KCl solution, left in contact with the solution with occasional stirring for 10 days, filtered, and the filtrate was titrated electrometrically to pH 6.8 with 0.02 *N* KOH. The soil on the filter paper was washed with the respective solutions until a portion of the filtrate gave a pH reading of 6.8. From 4 to 6 liters (the soils with low colloid fractions required less than 6 liters) of the solutions were used for saturation, in other words, complete replacement. The combined filtrates were titrated and the amount of 0.02 *N* KOH used was added to the amount of the titration on the first 250 cc. of the solutions. The "lime requirement", in terms of CaO, was calculated from the total amount of alkali.

The discrepancies in "lime requirement" between the two methods as shown in table 2 are large enough to raise the question of the reliability of the Veitch method, which depends on the contact of the soil with limewater. In a way the Veitch method approaches the replacement method, but the strong reagent used introduces side reactions; and besides, the replacement process

[3] The authors take this opportunity to express their indebtedness to Prof. A. W. Blair, who supplied the lime requirement data and placed at their disposal some of the soil samples.

could not be fully accomplished in the short interval of contact of the respective cation (Ca) with the soil. Because of this it is difficult with the Veitch method to obtain good checks on duplicate samples.

The Hopkins (4) method, which approaches still closer the replacement method for determining the "lime requirement," is open partially to the same criticisms as the Veitch method. According to the Hopkins method, the soil is treated with a neutral salt and the filtrate titrated; the titer is multipled by a certain factor (in one place the factor is 3, in another 4, and again 2.5) to give the lime requirement.

The other methods may also be criticised from the same standpoint.

TABLE 3

Replaceable hydrogen at various time periods of extraction

PLOT NUMBER	PLOT SOILS: Replacement hydrogen with N $BaCl_2$ extraction after			LABORATORY NUMBER	CHENANGO SOILS: Replaceable hydrogen with N $BaCl_2$ extraction after			N KCl extraction after	
	1 hour	1 day	10 days		1 hour	1 day	10 days	1 day	9 days
1914	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
7A	23.0	30.2	43.2	1	35.82	45.77	50.24	25.8	30.3
10A	25.1	31.9	33.1	2	56.66	62.66	65.33	64.0	71.7
11A	30.5	43.4	46.5	3	29.43	40.25	46.75	42.4	49.6
12A	20.0	26.6	34.6	4	33.13	36.04	38.37	57.0	63.3
1918									
7A	27.7	36.7	42.6	5	27.11	36.72	39.54	22.6	26.0
10A	20.8	27.0	36.2	6	31.57	39.47	39.47	40.0	60.0
11A	36.2	44.4	51.7	7	24.67	32.36	32.46	13.0	14.6
12A	16.0	25.0	32.3	8	23.8	33.33	33.33	33.0	33.0
1922									
7A	33.7	44.0	53.5	9	29.72	36.48	45.94	21.6	27.4
10A	26.2	30.0	37.3	10	23.45	24.69	29.62	20.8	30.8
11A	34.7	43.3	54.2	11	33.91	43.47	52.17	55.4	65.1
12A	18.4	30.5	39.6	12	46.15	73.07	73.07		

Table 3 shows how the percentage of replaceable hydrogen varies with each soil. The time of contact influences the release of the hydrogen ions, and the state of unsaturation is also an important factor.

The higher the state of unsaturation the faster the H ions are released. This is to be expected since the complex contains fewer of the other cations and the reaction is proceeding between the replaceable cations and the adsorbed H ions. For these reasons it is impossible to assign any definite factor which, when multiplied by the amount of alkali necessary to neutralize the acidity of a neutral salt solution extract in contact with the soil for any length of time, would give us the true lime requirement.

That the cations used in replacing the H ions have an influence on the speed

of replacement may be inferred from theoretical considerations; the bivalent cations with their higher coefficient of absorption and replacement ought to be more efficient in the replacement process. This has been found in general to hold true. There are, however, exceptions. The data on the relative speed of replacement by the Ba and K ions in table 3 on the Chenango soils show that the K ions replaced more H ions than the Ba ions in some samples. No explanation for such behavior can be offered. Surface relationships as influenced by the valency of the cations may enter as a factor.

At this point it will be of interest to look into the question raised by Gedroiz (3), whether the theoretical amount of lime requirement as calculated from the unsaturation of the soil coincides with the practical needs. The work of the New Jersey Agricultural Experiment Station on the limed (B) and unlimed (A) plots may offer a satisfactory explanation. The only difference in the treatment of the two series of plots is that the B plots receive an application of 2 tons of $CaCO_3$ every 5 years. The data on the yields from these

TABLE 4

Yield of dry matter—5-year period, 1918–1922

Calculated to acre basis

PLOT NUMBER	CORN—1918			OATS—1919		BARLEY—1920		TIMOTHY HAY 1921	TIMOTHY HAY 1921	TOTAL FOR 5 YEARS	INCREASE OVER CHECK
	Grain	Stalks	Cobs	Grain	Straw	Grain	Straw				
	pounds	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*	*pounds*
7B	2,329	1,746	404	680	1,280	568	752	650	960	8,689	Loss
8B	2,364	1,894	444	720	2,120	1,068	1,492	2,240	3,720	15,342	3,630
9B	2,316	2,406	397	440	2,440	1,244	1,796	2,960	5,040	18,599	6,887
10B	2,794	2,620	496	560	2,760	1,284	2,016	3,700	5,360	21,030	9,318
11B	2,714	2,406	478	720	2,680	1,360	2,120	3,620	4,680	20,058	8,346
12B	2,324	2,458	417	720	2,680	1,432	2,108	3,140	3,520	18,079	6,367

plots seem to indicate that such an application meets the requirements of the soil, even the one which receives as a fertilizer the acid-forming $(NH_4)_2SO_4$.

Table 4, compiled from the data on the crop yields of the plots is reported by Lipman, Blair and Prince (7), shows that 11B ranks in yield as high as any of the plots. For comparison the yields on several other plots are given in table 4. It is very possible that the low yield on the other plots is due to overliming, which probably depleted the complex from other bases and undoubtedly affected adversely the organic matter in the soil.

It may not be amiss at this point to recall that 11A, the unlimed plot corresponding to 11B, showed in 1922, just before the regular lime application was made, a lime requirement of about 2300 pounds of CaO.

A preliminary survey of the replaceable H ions in 11B shows that the complex contains replaceable H ions, even though the soil still contains carbonates of lime. This is in line with the ideas expressed by Gedroiz (3), but his fear of underliming is not well founded, as may be inferred from the

practical experiences at the New Jersey Station. It is doubtful whether a complete saturation with Ca ions would be desirable, for reasons pointed out on p. 130. The lime in the soil does not leach out to any extent and is present as a potential source, to release Ca ions into the soil solution to react with the solid phase of the complex.

SUMMARY

1. The relation of the various cations present in the soil complex (inorganic and organic) capable of base exchange is discussed.
2. The methods used in determining the base exchange capacity and the degree of unsaturation of soils are given.
3. The functions of the Ca ions in the soil-plant system are discussed from the standpoint of base exchange.
4. The relation between the state of unsaturation and the lime requirement is analyzed, and the experimental results are compared with methods for determining the lime requirement.
5. The degree of saturation and unsaturation in the layers of the soil profile indicates the possibility of utilizing subsoiling practice for the purpose of preserving the bases that are being leached out from the surface soils.
6. It is shown that an application of lime as indicated by the replacement method of lime requirement, is sufficient for the best results.

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A STUDY OF THE FACTORS INFLUENCING THE EFFICIENCY OF DIFFERENT FORMS OF NITROGEN AS RELATED TO SOIL TYPE AND CROPPING SYSTEM IN THE ATLANTIC COASTAL PLAIN REGION: PART I[1]

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Introduction

The economic utilization of nitrogen fertilizers is one of the outstanding problems of the market gardeners and truck farmers on the sandy soils of the Atlantic Coastal Plain. The Norfolk, Sassafras, Ruston, Keyport, and Elkton soils in particular contain relatively small amounts of nitrogen, and are usually coarse in texture. Since in many areas the subsoil contains even more sand than the surface soil, these soils are frequently subject to excessive leaching from both winter and summer rains. Especially in the tide-water regions of Maryland and Virginia, where the permanent water-table is close to the surface soil, large amounts of nitrogen are lost annually by leaching.

That the supply of available nitrogen is one of the important problems to farmers in the Atlantic Coastal Plain may be realized from the fact that an application of one ton per acre of a 7–6–5 or a 5–8–5 ($NH_3-P_2O_5-K_2O$) commercial fertilizer is the standard practice for early potatoes in many sections. These fertilizers cost on the average from $45.00 to $52.00 per ton. This has been estimated by economists of the United States Department of Agriculture (76) to be from 26 to 33 per cent of the total cost of producing this crop. For many other truck crops applications of from 1000 to 1500 pounds of similar fertilizers per acre are made.

Since the severe summer showers and heavy winter rains in this region tend toward the excessive leaching of nitrate nitrogen; the farmers have demanded large proportions of organic nitrogen materials in the mixed fertilizers, with a consequent increase in the basic cost of the same.

In this investigation an attempt is made to study some of the fundamental factors involved in the use of complete commercial fertilizers on these soils, with special reference to to the proportion of the nitrogen derived from inorganic and organic nitrogen fertilizer materials.

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[1] Summarized Introduction and Historical Review, of a Thesis submitted to the Graduate Faculty of the University of Maryland, June, 1925, in partial fulfillment of the requirements of the degree of Doctor of Philosophy. Part II is a detailed report on closely related field-plot experiments, and will be published at a later date with subsequent data.

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Historical

FACTORS INFLUENCING THE RATE OF NITRIFICATION

The effect of temperature on nitrification

The work of numerous investigators has shown that nitrification will take place in soils at all temperatures between 15° and 40°C. In particular, that of Jacobs, Allison and Braham (45), and of Panganiban (63) indicates that the optimum temperature is approximately 35°C.

The consensus of opinion from the work of Lemmerman and Wichers (50); Fraps (28); Whiting and Schoonover (80); Shonbrunn (70), Blair and Prince (10); Ģowda (35); and others, is that seasonal variations in the rate of nitrification are due largely to temperature, moisture, and other seasonal changes in the soil.

Moisture relations

Harris and Butt (40) found that a soil-moisture content of 23 to 28 per cent was optimum for nitrification. The work of Coleman (24), and of Jacobs, Allison and Braham (45) indicates that for most soils 50 to 60 per cent of the water-holding capacity is the optimum. Sachs and Austin (65), Albrecht (1), The Nebraska Agricultural Experiment Station (62), Munter (59), Carpenter and Bose (19), and Hall (38), all found that tillage practices designed to conserve moisture in field soils during the summer, increased the amount of nitrification.

Loss by leaching

The work of Garretson (32) and of Geilman (33) shows very little leaching of the ammonia form of nitrogen; most of the nitrogen lost in this manner being nitrate. Blair (10) found no more leaching when nitrate of soda was added to the soil used than when organic ammoniates were added. This brings up the question of soil texture and chemical composition in relation to the influence of sodium. Harrison (41) showed that a fairly heavy soil to a depth of 3 to 4 feet is necessary to prevent excessive leaching. The work of Wilson (81), and of Fraps (28) illustrates the value of crops and manures in conserving soil nitrates.

The previous work indicates that the leaching of soil nitrates is the resultant between the factors of soil texture, soil composition, climate, and the cropping and manuring systems.

The effect of soil reaction

The wide range of H-ion concentrations in soils in which nitrification is reported to have proceeded vigorously, leads one to believe that other soil factors such as moisture, temperature, buffer substances, i.e. organic matter, colloidal clay and zeolites, and microörganisms as well, may, in many instances, outweigh the influence of either an unfavorable OH- or H-ion concentration. This view is supported by the work of Fred and Graul (30), Garder and Hagum (31), Meek and Lipman (57), Barthel and Bengston (8), Fraps (28), Stevenson (73), Chardon-Placios (20), Blair and Prince (11), Shedd (69), Waksman (79), Munter (60), Murphy (61), Albrecht (3), and Denison (25).

For mineral soils the optimum reaction appears to be at about pH 7.0; although maximum values of OH-ion concentration of 13.0 and minimum values of pH 5.4 have been recorded. The work of Fraps (28), Murphy (61), and many others indicates that liming the soil favors nitrification; an exception being the work of Blair and Prince when using sulfate of ammonia as a fertilizer. Minimum values of pH 4.0 have been observed in peat soils. This is in line with Waksman's researches and explanation of the influence of various buffering materials.

The influence of salts on nitrification

The relation of salts to the nitrification process is of importance with respect to the influence of the non-nitrogenous fertilizer salts on the rate of availability of the nitrogen con-

tained in the fertilizer and also in the soil. Greaves (36) found that in alkali soils many salts increased the rate of nitrification. Erdman (27) found that normal applications of gypsum had no effect. Brown and Gowda (18) found that phosphates and nitrate of soda increased nitrification. The work of Fraps (28) on Texas soils showed phosphates to be more effective than potash in stimulating nitrifying bacteria. R. S. Smith (71) found that potassium sulfate stimulated and potassium chloride decreased the rate of nitrification.

Influence of the source of the nitrogen on nitrification

In the work of Jacobs, Allison and Braham (45) light applications of cyanamide were entirely nitrified in 5 days; and applications of 216 pounds per acre were completely transformed to nitrate in 10 days. They also found that small quantities of dicyano-diamide did not delay the nitrification of urea, but did delay the transformation of ammonium sulfate for 210 days. Littauer (54) found that urea was nitrified best in a loam soil; and, although drouth retarded the rate, increases in moisture above the average water capacity produced no essential changes in the rate of change to nitrate.

It is evident from the literature that the presence or absence of certain impurities in urea, as determined by the process of manufacture, largely determines the rate of nitrification.

Brenchley and Richards (16) found that all the nitrogen from finely divided dried blood was nitrified after 15 weeks. In the same time 26 per cent of that in slate-bed sewage sludge and 66 per cent of that in activated sludge has been changed to nitrate.

PLANTS AS INDICATORS OF THE AVAILABILITY OF NITROGEN FROM VARIOUS MATERIALS

So much experimental work has been published on various crops as indicators of nitrogen availability, that it is possible to cite only a few investigations bearing directly on some phases of the present problem, for example: the work of Schneidewind, Meyer and Munter (68); Hasselhof, Liehr and Fluhrer (42); Kuyper (48); Chevalier (21); Allison, Braham and McMurtey (4); Prescott (64); Allison, Vliet, Skinner, and Reid (5); Brenchley and Richards (16); Brown (17); Lemmerman and Eckl (49); Truffaut and Bezssonoff (74); Woods (83); Lipman and Blair (52); and Martin (56).

The consensus of opinion seems to be that crop response to different nitrogenous materials depends so largely on soil texture and composition, climatic factors, length of growing season and the root system of the crop, that no one material or type, of material is best adapted to all, or even to a large proportion of soils and crops. It has been largely a problem of determining the effects of these various influences on each nitrogen fertilizer, and thus learning its adaptability for any particular soil and crop combination.

The general conclusion seems to be that the water-soluble forms of nitrogen are best adapted to heavy soils and to short or cold growing seasons. For sandy soils, long growing seasons, and high soil temperatures, the soluble and insoluble organic nitrogen materials and the ammonia salts seem better adapted than the nitrate forms.

NITRIFICATION AS A MEASURE OF THE AVAILABILITY OF NITROGEN FOR PLANT GROWTH

According to the work of Bonazzi (13), and from a consideration of the processes for the synthetic production of ammonia and nitrates, the oxidation of ammonia in soils is accomplished by the catalytic activity of iron as part of a biological intracellular mechanism, through which the inert oxygen of the air is activated. Miyake and Soma (58) have shown that the process of nitrification as a whole resembles an autocatalytic mono-molecular bio-

chemical reaction; and that the increase of nitrates in soils is in accord with the formula for this type of reaction.

Hasselhof (42); Robinson, Winter, and Miller (65); and others, have shown that although the neutral and alkaline permanganate methods shed some light on the availability of insoluble, but easily hydrolyzable, organic nitrogenous compounds, they do not yield true values when compared with plant-culture experiments. The time consumed and the tedious processes involved make bacteriological and nutritional methods impractical for routine use in control laboratories. However, these latter methods are of real worth in establishng true values for the more rapid chemical methods in present use, or those to be devised in the future.

The work of Lipman and Burgess (51), Bizzell (9), Fraps (29), Waksman (78), and others, seems to show that nitrification tests under standard conditions are the best biological method for determining the availability of nitrogen in fertilizer materials; unless crop tests can be made under the soil and climatic conditions existing in the field where these materials are to be used. The results obtained by Lipman and Burgess (51) and by Waksman (78) in comparing ammonification and nitrification tests with crop growth experiments, seem to indicate that ammonification tests fail to yield real or consistent values over a wide range of conditions, such as exist in various field soils.

Although the writer is fully conversant with the work recently brought into prominence concerning the availability of the ammonia form of nitrogen to economic crop plants, he is inclined to agree with the findings of these investigators cited above. Although certain plants whose ecological habitat is found in wet, poorly drained, or very acid soils may be shown to take up appreciable quantities of nitrogen in the form of ammonia; the bulk of the evidence from practical farm experience, field plot experiments, pot culture studies, and bacteriological research shows that of the simple transformation products of organic nitrogen, nitrate is the only stable form in the soil; and that the proportion of nitrate to ammonia nitrogen found in most well drained soils proves conclusively that plants do absorb greater quantities of the nitrate form than of the ammonia form of nitrogen. For these reasons nitrification tests were adopted as the criterion of nitrogen availability in the present investigation.

Experimental

A COMPARISON OF VARIOUS NITROGENOUS FERTILIZER MATERIALS WITH RESPECT TO THE RATE OF NITRIFICATION AND THE LEACHING OF NITRATES FROM NORFOLK SANDY LOAM SOIL

The surface soil used in these experiments was secured from the experimental field at Snow Hill, Maryland. The data from preliminary mechanical and chemical analyses are given in table 1.

Sulfate of ammonia, urea, dried ground fish, high-grade packing-house tankage, and activated sewage sludge were compared with respect to their rate of nitrification in this soil. The urea was of the usual commercial grade now being sold in this country by the Badische Anilin und Soda Fabrik. The sulfate of ammonia, fish, and tankage were the usual commercial materials. The activated sewage sludge was obtained from Milwaukee, Wisconsin, the material having been produced by the method described by Kadish (46). Commercial nitrate of soda was used in the leaching experiments, and as a control on the nitrate absorption of the soil in the rate of nitrification studies.

In order to obtain an equitable basis for comparison, the organic materials were ground to approximately equal fineness, and to a degree possible under commercial conditions. Sieve tests were then made and the total nitrogen was determined, the results are shown in table 2.

Series I. The influence of soil moisture on the rate of nitrification

Each of the nitrogenous materials listed in table 2 was used in turn as the sole source of nitrogen in a complete fertilizer containing 7 per cent ammonia, 6 per cent phosphoric acid, and 5 per cent potash. In all cases the phosphorus and potassium were derived from 16 per cent acid phosphate and 50 per cent sulfate of potash, respectively. Of this fertilizer, 4-gm. portions containing

TABLE 1

Mechanical analysis determinations, Norfolk Sandy Loam

Mechanical analysis:*		
Fine gravel and coarse sand	*per cent*	16.0
Medium sand	*per cent*	31.8
Fine sand	*per cent*	36.4
Very fine sand	*per cent*	4.2
Silt	*per cent*	9.0
Clay	*per cent*	2.1
Water-holding capacity	*per cent*	27.1
Total nitrogen	*per cent*	0.041
H-ion concentration	pH	6.4
Lime requirement (Veitch method) 1500 pounds $CaCO_3$ per acre		

* Method of Bureau of Soils, U. S. Dept. Agr. (15).

TABLE 2

Analyses of nitrogenous materials used

MATERIALS	NITROGEN	MECHANICAL ANALYSIS					
		Coarser than 20 mesh	20–40 mesh	40–60 mesh	60–80 mesh	80–100 mesh	Finer than 100 mesh
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Dried ground fish	9.6	0.2	4.8	29.8	19.0	8.2	37.4
Packing house tankage	10.3	0.1	1.4	24.0	17.7	10.2	46.6
Sewage	5.1	...	2.0	37.2	16.9	8.4	35.5
Urea	45.3	...	...	....	....	....	....
Sulfate of ammonia	25.2	...	...	....	....	....	....
Nitrate of soda	14.9	...	...	....	....	....	....

230.4 mgm. of nitrogen each, were added to 4 kgm. of sifted air-dry soil contained in 1-gallon glazed pots. These additions correspond to a field application of 2000 pounds of fertilizer per acre.

The rate of nitrification of sulfate of ammonia, urea, fish, and tankage was compared at soil-moisture contents of 10, 20, 30, 40, 50, 60, and 70 per cent of the total water-holding capacity of the soil as determined by the Hilgard method (43-a). At the lowest moisture content, 108 gm. of water was added

TABLE 3

The effect of soil-moisture on the rate of nitrification

MOISTURE CONTENT	POT NUMBER	SOURCE OF NITROGEN	NITRATE-NITROGEN IN AIR-DRY SOIL							
			December 17	December 31	January 14	January 28	February 11	February 25	March 11	March 25
			0 days	14 days	28 days	42 days	56 days	70 days	84 days	98 days
			p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
10 per cent of water-holding capacity	1	Sulfate of ammonia	1.9	5.5	6.9	6.8	6.7	7.5	5.7	8.2
	2	Urea	0.6	5.6	7.1	6.5	7.1	7.5	8.2	11.1
	3	Dried ground fish	1.0	6.0	6.9	7.2	7.4	9.2	6.5	9.8
	4	Tankage	2.4	5.8	7.1	6.1	5.7	7.0	5.1	7.1
20 per cent of water-holding capacity	5	Sulfate of ammonia	1.9	2.6	7.2	12.4	21.4	30.1	22.7	41.7
	6	Urea	0.6	4.7	13.7	15.2	22.4	29.3	29.3	44.9
	7	Dried ground fish	1.0	5.4	11.1	14.7	20.4	19.6	26.8	27.1
	8	Tankage	2.4	5.1	11.1	14.9	27.6	21.2	28.3	31.3
30 per cent of water-holding capacity	9	Sulfate of ammonia	1.9	3.4	12.7	14.2	22.2	34.4	34.4	57.7
	10	Urea	0.6	4.3	16.4	27.8	32.2	37.9	43.4	52.1
	11	Dried ground fish	1.0	2.0	14.8	21.7	28.1	53.6	37.5	43.6
	12	Tankage	2.4	4.6	16.2	19.9	23.7	39.9	29.4	45.7
40 per cent of water-holding capacity	13	Sulfate of ammonia	1.9	2.9	14.8	25.9	36.8	41.7	40.1	37.5
	14	Urea	0.6	8.8	34.5	32.0	36.8	54.0	36.2	30.0
	15	Dried ground fish	1.0	4.5	13.2	24.4	37.5	53.6	34.3	47.8
	16	Tankage	2.4	5.6	18.5	27.4	38.3	50.0	31.3	49.3

50 per cent of water-holding capacity	17	Sulfate of ammonia	1.9	6.1	17.8	30.5	49.3	58.6	45.7	73.5
	18	Urea	0.6	6.5	19.8	35.4	59.5	67.0	21.3	51.7
	19	Dried ground fish	1.0	4.0	15.8	25.5	47.9	47.5	35.4	37.5
	20	Tankage	2.4	6.8	18.7	28.2	46.6	52.8	28.9	22.7
	21	Nitrate soda	65.2	20.3	73.5	69.5	80.7	85.2	35.7	60.0
	22	Sewage	1.7	5.2	17.6	25.0	28.6	33.3	21.3	30.6
	23	0–6–5	1.9	6.3	13.7	15.8	14.7	19.9	12.3	16.0
60 per cent of water-holding capacity	24	Sulfate of ammonia	1.9	5.8	18.7	37.9	48.7	65.8	53.6	51.7
	25	Urea	0.6	7.4	31.1	66.4	62.5	76.5	60.0	62.5
	26	Dried ground fish	1.0	7.7	17.5	41.2	41.4	56.8	29.3	44.1
	27	Tankage	2.4	7.1	20.9	40.1	39.5	50.3	21.1	40.5
70 per cent of water-holding capacity	28	Sulfate of ammonia	1.9	7.8	20.0	42.9	37.5	54.0	45.2	32.1
	29	Urea	0.6	6.8	29.9	67.0	49.3	67.0	69.5	69.5
	30	Dried ground fish	1.0	5.1	17.3	42.9	41.4	44.1	48.4	27.3
	31	Tankage	2.4	7.3	20.6	40.3	37.1	41.9	43.4	28.2
Mean air temperature			°C.	14.0	15.1	16.1	18.0	17.1	18.1	18.0
			°F.	57.1	59.7	61.8	64.1	63.3	64.8	63.9

to 4000 gm. of soil, while at the highest, 761 gm. of water was added. The experiment was conducted in the greenhouse for a period of 98 days from December 17 to March 25, during which time the pots were neither covered nor shaded. The pots were weighed twice each week, and distilled water was added to replace the loss by evaporation. After each sampling the soils were cultivated to a depth of ½ inch.

At 50 per cent of the water-holding capacity three additional fertilizer treatments were employed. In one of these, activated sludge was used as the nitrogenous material. Another, in which nitrate of soda was used, served as a control pot for measuring nitrate absorption by the soil and the utilization of nitrates by soil organisms. The third, to which no nitrogen was added, served as a control to measure the rate of nitrification of the original soil nitrogen.

In order to obtain representative samples, borings from the top to the bottom of each pot were made at 14-day intervals. Seventy-gram samples of the moist soil were dried in the oven at 50°C. for 15 hours, and 50-gram portions

TABLE 4

Time-periods required for the nitrate nitrogen to equal the total nitrogen applied in the fertilizer

MATERIALS	SOIL-MOISTURE AS PER CENT WATER-HOLDING CAPACITY						
	10 per cent	20 per cent	30 per cent	40 per cent	50 per cent	60 per cent	70 per cent
	days	*days*	*days*	*days*	*days*	*days*	*days*
Sulfate of ammonia	....	....	98	....	70	70	70*
Urea	....	....	98*	70*	56	42	42
Dried ground fish	....	....	70*	70*	....	70	....
Packing house tankage	....	....	....	70*	70*	70*	....

* Amounts slightly less than 57.6 p.p.m.

of the dried soil were then extracted with 250 cc. of distilled water. Nitrates were determined throughout by the phenol-disulfonic acid method as modified by Harper (39).

The results of the nitrate determinations for each 14-day period are shown in table 3, in which the nitrate-nitrogen is expressed as parts per million of air-dry soil.

An inspection of table 3 shows that, in general, for the first 42-day period the rate of nitrification increased in direct proportion to the increase in soil moisture. For the 42 to 98-day period there was a direct increase in nitrification with increasing soil moisture up to 50 per cent of the water-holding capacity of the soil, except in the case of urea, which yielded a high nitrate content at both 60 and 70 per cent of the water-holding capacity.

At the lowest moisture content very little nitrification took place from any of the materials added. At the 20 per cent level and, in fact, at all of the higher moisture contents, urea and sulfate of ammonia nitrified more rapidly and gave higher nitrate accumulations than either fish or tankage.

Considerable variation in the nitrate accumulation for all of the materials may be noticed at the higher soil moisture contents after the 56-day period. This periodicity during short intervals has been noted by numerous investigators. Löhnis in particular (54) has observed similar fluctuations due to biological factors, such as the utilization of nitrates by microörganisms other than the nitrate bacteria. In the present experiment the fluctuations cannot be explained satisfactorily on the basis of differences in soil moisture, temperature, or H-ion concentration, and accordingly are probably due to nutritional differences caused by the various rates of decomposition of the soil organic matter as influenced by the decomposition products and the nitrification of the materials added.

The theoretically possible concentration of nitrate nitrogen as calculated from the total nitrogen contained in the soil and fertilizer, is 467.6 p.p.m., of which 57.6 p.p.m. was added in the fertilizer. It is interesting to observe for the various soil-moisture contents the time required with the different materials for the nitrate-nitrogen to equal the nitrogen added in the fertilizer. These observations are presented in table 4.

From this summary it may be noted that in this soil, under the conditions of the experiment, the optimum soil-moisture content for the nitrification of these four materials lies between 50 and 60 per cent of the water-holding capacity. It will also be noted that a greatest total nitrate accumulation occurred at somewhat higher moisture contents for sulfate of ammonia and for urea than for either fish or tankage. The rate of nitrification in this soil at moisture contents of 30 per cent of the water-holding capacity or less is exceedingly slow. Of the four materials, urea nitrified most readily, and, with the exception of nitrate of soda and of sulfate of ammonia at certain moisture contents, gave the highest accumulation of nitrates.

It is not to be supposed that all of the nitrate-nitrogen was derived from the fertilizer materials. The work of R. S. Smith (71), Gowda (35), and others has shown that both phosphates and potassium salts stimulate nitrification of the original nitrogen contained in the soil. Table 3 shows numerous instances of nitrate accumulation greater than the amount of nitrogen supplied in the fertilizer. It is interesting to note that pot 27, which received nitrate of soda, showed not only the greatest accumulation of nitrate nitrogen, but also the largest excess over that supplied in the fertilizer. This shows a direct stimulation of nitrification by this material. The fluctuation in nitrate nitrogen in this pot at the different time intervals would indicate that nitrate of soda also stimulated the growth and activity of the other soil organisms.

After the first 28 days at 50 per cent of the water-holding-capacity of the soil, the nitrification of sewage sludge took place very slowly. After the first 14 days, the pot receiving phosphate and potash only had a much lower nitrate content than any of those receiving nitrogenous fertilizers.

The H-ion concentration of the soil as determined colorimetrically at the beginning of the experiment was pH 6.4. There was no noticeable difference

TABLE 5

The effect of soil temperature on the rate of nitrification

	POT NUMBER	SOURCE OF NITROGEN	NITRATE-NITROGEN IN AIR-DRY SOIL							
			December 17	December 31	January 14	January 28	February 11	February 25	March 11	March 25
			0 days	14 days	28 days	42 days	56 days	70 days	84 days	98 days
			p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
Cold room	44	Sulfate of ammonia	1.9	3.4	11.2	9.7	10.4	15.8	39.7	49.0
	45	Urea	0.6	3.4	9.9	10.3	10.5	18.8	48.4	63.0
	46	Dried ground fish	1.0	1.9	13.2	8.8	10.5	16.7	41.0	45.7
	47	Tankage	2.4	2.4	10.7	10.3	11.8	19.2	41.0	48.7
	48	Sewage	1.7	2.5	9.5	9.7	11.0	18.3	31.9	28.9
	49	0–6–5 check	1.9	3.5	11.2	10.8	12.4	13.6	17.1	14.4
Shaded green house	32	Sulfate of ammonia	1.9	3.9	14.1	36.8	37.9	56.4	44.4	75.0
	33	Urea	0.6	5.1	25.8	50.0	50.3	62.5	62.0	73.5
	34	Dried ground fish	1.0	5.5	16.9	39.9	36.4	51.4	48.1	61.5
	35	Tankage	2.4	5.6	20.4	37.1	37.9	58.6	44.9	79.0
	36	Sewage	1.7	7.4	20.8	30.5	31.3	32.6	35.1	34.9
	37	0–6–5 check	1.9	2.8	14.4	18.5	14.9	24.8	18.3	22.1
Not shaded green house	17	Sulfate of ammonia	1.9	6.1	17.8	30.5	49.3	58.6	45.7	73.5
	18	Urea	0.6	6.5	19.8	35.4	59.5	67.0	21.3	51.7
	19	Dried ground fish	1.0	4.0	15.8	25.5	47.9	47.5	35.4	37.5
	20	Tankage	2.4	6.8	18.7	28.2	46.6	52.8	28.9	22.7
	21	Nitrate soda	65.2	20.3	73.5	69.5	80.7	35.2	35.7	60.0
	22	Sewage	1.7	5.2	17.6	25.0	28.6	33.3	21.3	30.6
	23	0–6–5 check	1.9	6.3	13.7	15.8	14.7	19.9	12.3	16.0

Warm rose house	38	Sulfate of ammonia	1.9	4.7	19.3	52.5	54.8	52.5	70.1	117.2
	39	Urea	0.6	5.9	29.8	75.0	70.8	75.0	81.5	61.0
	40	Dried ground fish	1.0	3.2	23.3	48.1	50.7	50.0	65.2	79.8
	41	Tankage	2.4	6.8	29.2	51.7	50.7	49.3	57.7	90.4
	42	Sewage	1.7	6.7	22.3	41.7	35.7	41.0	30.5	60.0
	43	0–6–5 check	1.9	6.3	11.7	18.6	23.8	20.8	12.5	26.1
Mean air temperature (main greenhouse)			°C.	14.0	15.1	16.1	18.0	17.1	18.1	18.0
			°F.	57.1	59.7	61.8	64.1	63.3	64.8	63.9

in the H-ion concentration after 98 days with respect to the various moisture contents. In the soil receiving the fertilizer containing sulfate of ammonia, the initial H-ion concentration was pH 6.0. After 98 days the average pH values for the soils receiving the various sources of nitrogen were: sulfate of ammonia, 5.6; urea, 5.7; fish and tankage, 5.9. As might have been predicted from the mechanical analysis, given in table I, the buffer action of this soil is relatively low. The temperature relations will be discussed in connection with the next series of experiments.

Series II. The influence of soil temperature on the rate of nitrification

The duration, periods of sampling, containers, weight and type of soil employed, and the analysis and rate of application of the fertilizer were the same in Series II as in the preceding series.

The following materials were used as the sole source of nitrogen in the 7–6–5 complete fertilizer: sulfate of ammonia, urea, dried ground fish, packing-house tankage, and activated sewage sludge. A check treatment of phosphate and potash only was included in each group. To each pot, water was added to 50 per cent of the water-holding capacity of the soil, and the loss by evaporation was replaced twice each week.

Four groups of 6 pots each, treated as indicated above, were kept for 98 days at different temperatures. The first group, pots 44 to 49 as shown in table 5, was kept in a cold room, which received daylight through several windows. The second group, pots 32 to 37, was kept on a shelf under a stone-top table in the main greenhouse and was protected at all times from the warming effect of direct sunlight. The third group, pots 17 to 23, was placed in the main greenhouse and exposed to sunlight. This group is included in Series I as the 50 per cent water-holding capacity treatment. The fourth group, pots 38 to 43, was placed in a rose greenhouse where the temperature was maintained at a higher and more uniform temperature than in the house first mentioned.

No attempt was made to control the temperature of the soils, but frequent thermometer readings showed the following temperature conditions. The soil-temperature in the cold room ranged during the first 56 days from 3° to 12°C., and for the last 42 days from 12° to 17°C. The mean temperature for each bi-weekly period in the main greenhouse as recorded by a thermograph, is given at the foot of tables 3 and 5. The weekly average of the maximum air temperatures ranged from 17.5° to 27°C., and the weekly average minimum from 7° to 13°C., giving an average diurnal change of 10.5° to 13°C. The soil temperatures, of course, did not undergo either of these extreme fluctuations, having at most times a lag of 3 to 5°C. for rising and falling temperatures. The soil in pots 32 to 37 shaded by the stone-top table was at all times during sunny days from 2° to 3°C. cooler than pots 17 to 23 placed on top of the wooden table. The soils in pots 38 to 43 in the warmer greenhouse averaged at all times from 3° to 5°C. warmer than pots 17 to 23 in the main

unshaded greenhouse. During periods of exceedingly cold weather these soils frequently had a temperature 8°C. higher than those of the main greenhouse.

The object in comparing the rates of nitrification of these materials at different temperature levels was to ascertain, if possible, their adaptation for both early and midseason crops.

The results of the nitrate determinations at successive 14-day intervals are shown in table 5.

It may be seen from the data that in the pots placed in the cold room, the rate of nitrification during the first 70 days was slow for all of the nitrogenous materials employed, being at the most only 50 per cent more than for the soil alone. There was, however, a gradual nitrate accumulation at this low temperature level. During the last 28 days, as the temperature increased with the rising outdoor temperatures, there was an appreciable nitrate accumulation in all cases, equaling with some of the materials, the amounts shown in the main greenhouse where higher temperatures prevailed. The rapidity of nitrification at this low temperature level was in the following order: urea, then tankage, sulfate of ammonia, and fish closely grouped, activated sewage sludge, and no applied nitrogen. These results would indicate that urea might have a slight advantage over the other materials as a source of nitrogen for early spring or winter crops.

A comparison of the data for the shaded and unshaded soils in the main greenhouse shows considerable variation in the effect of the shading. Although in general the slightly higher temperatures resulting from the exposure to sunlight induced a slightly more rapid nitrification at the start, and with the exception of the activated sewage sludge, yielded a higher nitrate accumulation at the 56-day period, the influence of the slight temperature difference is not consistent. Of two possible explanations one is, that the greater loss of water by evaporation from the group exposed to sunlight may have offset the advantage of the slightly higher temperature attained. In Series I it is shown that 50 per cent of the moisture holding capacity approaches the lower limit of the optimum water content for nitrification in this soil. Accordingly, the more rapid evaporation would not provide more favorable moisture relations or stimulate nitrification through increased soil aeration.

In view of the data for Series I, however, in which there was a fluctuation in the nitrate accumulation from these materials at all soil-moisture levels of 30 per cent of the water-holding capacity and higher, and under the same temperature range as for numbers 17 to 23, the explanation does not seem to lie in a difference in moisture content. It will be observed that the nitrate accumulations in the soils exposed to sunlight showed more extreme fluctuations than those in the shaded soils, although the variations in the two groups agree in general with respect to the time periods of sampling. From the data it appears that the slightly higher temperatures attained during sunny days in the group exposed to sunlight, stimulated the growth and activity of the entire microbiological flora of this soil, to the extent of utilizing a larger portion

of the accumulated nitrates, than was the case in the shaded soils. This hypothesis is strengthened by the fact that for practically every treatment in the shaded, as well as in the unshaded soils, there was an actual *decrease* in nitrate accumulation at the end of the bi-weekly periods during which there was an *increase* in the mean temperature. Thus there was very little increase in nitrate accumulation in the shaded soils from the 42- to the 56-day period during which time there was an increase in mean temperature of 1.9°C. Although the soils exposed to sunlight showed a consistent accumulation of nitrates from all the materials under comparison for the first 70 days, during the next 14-day period there was a decided decrease in nitrates in both the shaded and unshaded soils. At the same time the mean temperature increased 1.0°C. During the final 14-day period immediately following, there was again a marked increase in nitrate accumulation in both shaded and unshaded soils in nearly every case, while the mean temperature remained practically constant.

That this fluctuation in nitrate accumulation is due to the utilization of nitrates by soil microörganisms, as stimulated by a slightly increased mean temperature, is further indicated by referring in table 3 to the analyses at the 84-day period. The nitrate accumulations from urea, fish, and tankage at soil moisture levels of 30 and 40 per cent of the moisture-holding capacity equaled or exceeded the accumulations from the same materials during the same time in the soils moistened to 50 per cent, and, for some materials, to 60 per cent of the moisture-holding capacity. This would indicate that the fluctuations in the amounts of nitrate accumulations were not due to the more rapid evaporation of water at the slightly higher mean temperature levels. It may also be observed from table 3 that increasing mean temperatures did not offset the unfavorable conditions due to supra-optimum moisture relations in the group of soils moistened to 70 per cent of the water-holding capacity. Had the loss of water by evaporation been the cause of the fluctuations observed, these soils should have undergone an increase, rather than a continued decrease, in nitrate content during the final 28 days. In fact the amounts of moisture lost were practically negligible, in view of the weight of soil employed—4000 gm.— and of the semi-weekly additions of water.

In considering the data from the soils in the warm greenhouse it will be noticed that the fluctuations in accumulated nitrates are less evident and more irregular than for the soils kept in the main greenhouse. It will also be noticed that the time periods of fluctuation in nitrate accumulation do not coincide closely with those of the other soils. This might be expected, as there was very little correlation between the climatic factors existing in the two greenhouses. In the latter, used chiefly for the winter forcing of roses, a uniformly warm temperature was maintained. It may be observed from table 5 that in practically every case the rate of nitrification and nitrate accumulation was greater for the same materials at the same time intervals at these higher temperatures (by 3° to 5°C.), than in the main greenhouse at the lower tem-

peratures. This clearly shows the favorable influence of increased temperatures on nitrification.

It should be observed that in no case did the temperatures attained in these studies reach the optimum temperatures of 30° to 35°C. for nitrification as reported by Jacob, Allison and Braham (45), and by Panganiban (63). The purpose of this experiment was to compare at rather low soil temperatures the rate of nitrification of the nitrogen supplied by these materials, in order to simulate, as far as possible, the temperature conditions existing in field soils of this type at the time of planting early truck crops. The soil-temperatures of the experimental field at Snow Hill, Maryland, were recorded by thermographs during the growing season of 1924, for which the data on crop yields are included in part II of this paper.

For consecutive 14-day periods up to a total of 70 days from the date of planting early potatoes, the bi-weekly mean temperatures of the field soil at a depth of 6 inches were 5°, 6°, 3.5°, 2°, and 1°C. less than those recorded for corresponding periods in the main greenhouse. The other factors encountered in field conditions will be discussed in connection with the field-plot data.

Although the nitrogen from tankage nitrified slightly *more rapidly* than from fish at the higher temperatures, the nitrate accumulation from these two materials does not seem consistently different. Urea nitrified *more rapidly* than any of the other materials compared, except at the lowest temperature level, for which, however, it gave the highest nitrate accumulation after 84 days.

Sulfate of ammonia nitrified less rapidly than urea, fish, or tankage during the first 4 to 6 weeks. At the higher temperatures, however, it nitrified more rapidly than did the activated sewage sludge. Attention is called in table 3 to the high nitrate accumulation from sulfate of ammonia at the end of the 98-day period. There was a direct correlation between the nitrate accumulation from this material and the H-ion concentration, the lowest pH value, 5.2, accompanying the maximum nitrate content from the sulfate of ammonia treatment. An interesting problem is suggested regarding the permanence of the nitrate accumulations from sulfate of ammonia with respect to the effect of low pH values on the utilization of nitrates by soil microörganisms.

In general after the first 28 days the activated sewage sludge nitrified more slowly than the other nitrogenous materials and produced a lower nitrate accumulation. At the lowest temperature level, however, it compared favorably with all of the materials employed, while at the highest temperature level it ultimately gave a nitrate accumulation comparable with that from the other materials, with the exception of sulfate of ammonia. In view of the fact that many of the favorable results reported for this material were obtained in northern states and in Canada, the data from these studies may be significant in indicating its value as an organic nitrogenous material in cold climates and in cool growing seasons. On the other hand the slow but steady response obtained at the highest temperature level would suggest a definite value for

activated sludge under midseason conditions. Its low nitrogen content, 5.1 per cent, is unfavorable for its utilization as a source of nitrogen in fertilizer mixtures, but its excellent mechanical condition and drying properties would suggest a definite value as a conditioner and auxiliary source of nitrogen. Inasmuch as this material consists very largely of dried and reversible organic colloids, the gradual rate of nitrification may be closely related to the colloidal property of the activated sewage sludge. Further investigations with this material are being conducted under field conditions, and the colloidal phase of the problem will be studied in more detail.

The amount of nitrogen added to these soils, as in Series I, was equivalent to 57.6 p.p.m. It will be noticed in table 5 that at the lowest temperatures, and up to the end of the 98-day period only one material, urea, had produced this amount of nitrate nitrogen. In the shaded soils in the main greenhouse, urea, tankage, sulfate of ammonia, and fish in the order named had produced practically this amount in 70 days. At the highest temperature level, after 42 days the added nitrogen was equaled in amount by the nitrate nitrogen produced from all the materials compared, except activated sewage sludge.

In comparison with soil-nitrification studies as reported by Fraps (29), and others, in which the maximum amount of nitrate formation took place within the first 4 weeks, the relatively slow rates of nitrification shown by this soil during the early weeks and the high nitrate accumulations in the later periods, are worthy of notice. Not only were the temperature levels employed lower than usually has been the case in such studies, but the bacterial population of this soil is comparatively low. The low content of total organic matter, and the porous drouthy conditions observed in the field, explain this deficiency. The work of Bonazzi (13) on the mechanism of nitrification would indicate that a carbon dioxide deficiency in the early stages may possibly have retarded the rate of nitrification.

With respect to H-ion concentration there was no observable correlation with the differences in mean temperatures. With the exception of sulfate of ammonia, which invariably decreased the pH values, the various materials gave only inconsistent and inconsequential differences in soil reaction.

Series III. The leaching of nitrates as influenced by various nitrogenous materials

The duration, the periods of sampling, the soil, and the analysis and rate of application of the fertilizer were the same in Series III as in Series I and II. Twelve glass percolation cylinders 7 inches in diameter by 14 inches in depth and slightly conical in shape, were used as containers. These were enclosed in a large wooden case 12 by 135 by 14 inches, as shown in figure 1.

To insure adequate drainage at the outlet and to prevent the loss of soil, 60 gm. of quartz gravel, the size of small marbles, was placed in the bottom of each cylinder and upon this was placed a layer of fine gravel. Each of the cylinders were then filled with 5500 gm. of sifted air-dry soil. The soil was moistened and leached six times between the dates of October 29 and November

26, to insure uniform drainage conditions. The leachings of November 26 contained an average of 4.3 mgm. of nitrate nitrogen. The top 3 inches—1000 gm.—of the soil was then removed from each cylinder and air-dried, after which it was thoroughly mixed with 5.5 gm. of 7–6–5 fertilizer and returned to the percolators. The fertilizer was mixed with the surface 3 inches of soil, rather than with the entire mass, to prevent mechanical loss from washing. The soil was then moistened by the addition of 200 cc. of distilled water and at 14-day intervals thereafter, the entire mass was leached with 825 cc. of distilled water added slowly to each cylinder. The volume of leachings obtained from each is shown in table 8. Calculated on the acre-inch basis for rainfall, and on the assumption that the weight of one acre of surface soil is 2 million pounds, these additions approximate a bi-weekly rainfall of $1\frac{1}{2}$ inches. Three days

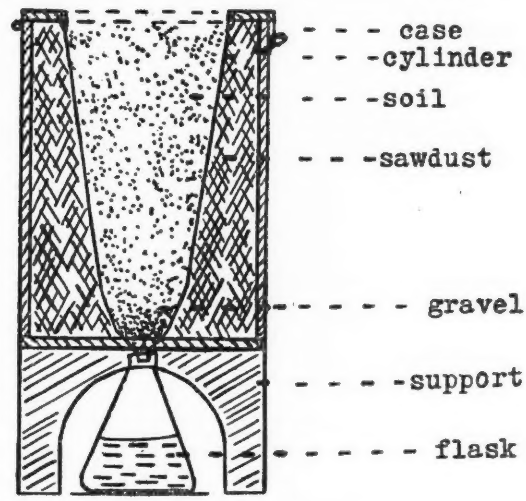

FIG. 1. DIAGRAMMATIC CROSS-SECTION OF CYLINDER AND CASE

after each addition of water the soil in each cylinder was cultivated to a depth of $\frac{1}{2}$ inch.

The application of 5.5 gm. of fertilizer to 5500 gm. of soil corresponds to a field application of 2000 pounds per acre of the fertilizer mixture, which contains the equivalent of 115.2 pounds of nitrogen. In each mixture all of the phosphorus was derived from 16 per cent acid phosphate and all of the potassium from potassium sulfate. Nitrate of soda, sulfate of ammonia, dried ground fish, and packing-house tankage were used singly and in combination as the sources of nitrogen. The various proportions of nitrogen carriers used for each cylinder are given in tables 6 and 7. In the fertilizers containing all four of these nitrogenous materials, the inorganic nitrogen was supplied in equal amounts by nitrate of soda and sulfate of ammonia, and the organic

TABLE 6

Nitrogen (as nitrate) leached at 14-day intervals with totals to date

(Nitrogen added in fertilizer 316.6 mgm.)

NUMBER	SOURCE OF NITROGEN IN 7-6-5 FERTILIZER*	DECEMBER 31 14 DAYS		JANUARY 14 28 DAYS		JANUARY 28 42 DAYS		FEBRUARY 11 56 DAYS		FEBRUARY 25 70 DAYS		MARCH 11 84 DAYS		MARCH 25 98 DAYS		APRIL 8 112 DAYS	
		Leached	Total	Leached	Total	Leached	Total	Leached	Total	Leached	Total	Leached	Total	Leached	Total	Leached	Total
		mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
1	Nitrate of soda	62.8	62.8	186.4	249.2	68.8	318.0	22.4	340.4	6.9	347.3	3.6	350.9	3.1	354.0	5.1	359.1
2	Sulfate of ammonia	21.5	21.5	78.5	100.0	84.9	184.9	51.2	236.1	14.9	251.0	6.4	257.4	4.5	261.9	5.6	267.5
3	Dried ground fish	15.9	15.9	68.8	84.7	68.6	153.3	51.8	205.1	21.1	226.2	16.8	243.0	10.0	253.0	10.8	263.8
4	Urea	25.1	25.1	105.0	130.1	76.2	206.3	40.5	246.8	9.1	255.9	5.2	261.1	4.7	265.8	6.7	272.5
5	Packing house tankage	21.8	21.8	76.1	97.9	71.8	169.7	39.2	208.9	20.5	229.4	12.8	242.2	8.1	250.3	10.8	261.1
6	½ nitrate; ½ sulfate	79.3	79.3	127.6	206.9	74.3	281.2	30.0	211.2	9.8	321.0	5.5	326.5	4.2	330.7	6.2	336.9
7	40 per cent inorganic; 60 per cent organic	45.4	45.4	87.2	132.6	74.2	206.8	41.9	248.7	16.8	265.5	10.9	276.4	8.4	284.8	9.4	294.2
8	50 per cent inorganic; 50 per cent organic	55.7	55.7	106.4	162.1	54.4	216.5	42.7	259.2	15.8	275.0	11.6	286.6	6.1	292.7	8.2	300.9
9	60 per cent inorganic; 40 per cent organic	39.4	39.4	94.5	133.9	63.5	197.4	37.9	235.3	14.8	250.1	9.1	259.2	6.0	265.2	6.8	272.0
10	70 per cent inorganic; 30 per cent organic	43.1	43.1	127.6	170.7	67.4	238.1	37.0	275.1	12.6	287.7	7.5	295.2	7.3	302.5	6.9	309.4
11	80 per cent inorganic; 20 per cent organic	30.1	30.1	171.8	201.9	72.4	274.3	42.0	316.3	9.9	326.2	5.4	331.6	4.1	335.7	5.7	341.4
12	Check—0-6-5	15.4	15.4	19.7	35.1	6.9	42.0	8.4	50.4	3.6	54.0	5.1	59.1	3.1	62.2	5.3	67.5

* 5.5 gm. fertilizer per 5500 gm. soil.

nitrogen, in equal amounts by fish and tankage. Except for cylinder 4, in which urea was used as the sole source of nitrogen, these mixtures and rates of application are exact duplicates of those employed in the field-plot experiments.

Table 6 gives the milligrams of nitrate nitrogen leached at each 14-day interval with the total amounts to date. Table 7 gives the same information in terms of percentage of the added nitrogen leached to date at the end of each 14-day interval. Table 8 is included merely to show the drainage conditions which existed at each date of leaching throughout the total period of 112 days.

TABLE 7

Proportion of added nitrogen leached at 14-day intervals

(825 cc. distilled water—equivalent to 1.5 inches rainfall added every 14th day)

NUMBER	SOURCE OF NITROGEN IN 7–6–5 FERTILIZER	DECEMBER 31 14 DAYS	JANUARY 14 28 DAYS	JANUARY 28 42 DAYS	FEBRUARY 11 56 DAYS	FEBRUARY 25 70 DAYS	MARCH 11 84 DAYS	MARCH 25 98 DAYS	APRIL 8 112 DAYS
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	Nitrate of soda	15.0	67.6	87.2	91.6	92.6	92.2	92.2	92.1
2	Sulphate of ammonia	1.9	20.5	45.1	58.6	62.2	62.6	63.1	63.2
3	Dried ground fish	0.2	15.7	35.2	48.9	54.4	58.1	60.3	62.0
4	Urea	3.1	30.0	51.9	62.0	63.8	63.8	64.3	64.8
5	Packing house tankage	2.0	19.8	40.3	50.1	55.4	57.9	59.4	61.1
6	½ nitrate; ½ sulfate	20.2	54.3	75.6	82.4	84.3	84.5	84.8	85.1
7	40 per cent inorganic; 60 per cent organic	9.5	30.8	52.1	62.6	66.8	68.6	70.3	71.6
8	50 per cent inorganic; 50 per cent organic	12.7	40.1	55.1	66.1	69.8	71.8	72.8	73.7
9	60 per cent inorganic; 40 per cent organic	7.6	31.2	49.1	58.4	61.9	63.2	64.1	64.6
10	70 per cent inorganic; 30 per cent organic	8.7	42.8	61.9	71.0	73.8	74.6	75.9	76.4
11	80 per cent inorganic; 20 per cent organic	4.6	52.7	73.4	84.0	86.0	86.1	86.4	86.5
12	Check 0–6–5 (subtracted in each case for the corresponding period)								

* 5.5 gm. fertilizer per 5500 gm. soil.

The original soil contained 0.041 per cent of total nitrogen, or 2.255 gm. in each cylinder, to which was added 0.3166 gm. in the fertilizer mixture. From table 6 it may be observed that after subtracting the amount leached from the checks, the total amount of nitrate-nitrogen recovered after 112 days was in no case equal to that added in the fertilizer. Other investigators have shown that soluble salts of phosphorus and potassium stimulate the nitrification of the nitrogen of the soil. A comparison of the 4.3 mgm. of nitrate-nitrogen per cylinder, obtained from the last leaching prior to the addition of the fertilizer, with the amounts shown for cylinder 12 at the 14- and 28-day

periods, indicates a marked stimulation of nitrification by the acid phosphate and potassium sulfate. A part of this stimulation must be ascribed, however, to the thorough aëration of the portion of soil removed for mixing with the fertilizer.

It must be recognized that not all of the nitrogen leached from any one of the cylinders came from the fertilizer. In the two series just described, there were a number of instances in which the nitrate accumulation exceeded the amount of added nitrogen plus the nitrate accumulation in the soils receiving phosphate and potash only. This indicates that the nitrification of the soil nitrogen was stimulated by the nitrogenous materials as well as by the phosphorus and potassium salts. Even though the nitrate leached from any of the cylinders

TABLE 8

Total volume of leachings at various time intervals

NUMBER	TREATMENT	14 DAYS	28 DAYS	42 DAYS	56 DAYS	70 DAYS	84 DAYS	98 DAYS	112 DAYS
		cc.	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*
1	Nitrate of soda	295	705	1,195	1,730	2,172	2,517	2,700	3,068
2	Sulfate of ammonia	420	985	1,433	1,988	2,455	2,871	3,179	3,574
3	Dried ground fish	392	962	1,467	2,047	2,449	2,891	3,176	3,523
4	Urea	379	949	1,324	1,919	2,329	2,692	2,970	3,325
5	Packing house tankage	345	910	1,355	1,892	2,327	2,737	2,997	3,342
6	½ nitrate; ½ sulfate	410	1,008	1,522	2,079	2,557	2,980	3,290	3,698
7	40 per cent inorganic; 60 per cent organic	445	1,013	1,476	2,063	2,546	2,976	3,299	3,652
8	50 per cent inorganic; 50 per cent organic	397	947	1,352	1,928	2,332	2,762	3,009	3,376
9	60 per cent inorganic; 40 per cent organic	394	939	1,297	1,762	2,126	2,481	2,729	3,029
10	70 per cent inorganic; 30 per cent organic	365	901	1,273	1,763	2,143	2,507	2,783	3,088
11	80 per cent inorganic; 20 per cent organic	445	975	1,337	1,862	2,262	2,687	2,989	3,333
12	No nitrogen	358	914	1,292	1,857	2,222	2,670	2,890	3,220

receiving nitrogen did not exceed that leached from the check cylinder by the amount added, it is evident that a part of the soil nitrogen was leached and that a part of the added nitrogen was utilized by soil microörganisms. A clearer comparison of the various materials is obtained, however, by subtracting the nitrate leached from the check cylinder at each time period, from that leached from each of the other cylinders, and by expressing the net amounts as percentages of the nitrogen added in the fertilizer.

Table 7 shows in general that the rapidity of leaching and the amount of nitrates lost in the drainage water vary directly with the proportion of the nitrogen supplied by nitrate of soda. Conversely the greater the proportion of organic ammoniates, the slower was the rate of leaching and the smaller the total amounts lost during the 112-day period. From cylinders 1, 6, and 11,

to which the nitrogen was added in the forms of nitrate of soda, of the 50–50 ratio nitrate of soda and sulfate of ammonia, and of the 80–20 ratio respectively, more than 50 per cent of the added nitrogen was leached at the first two periods, i.e. by 3 inches of rainfall. By the third period the equivalent of 50 per cent or more of the added nitrogen had been leached from the soils receiving nitrogen as urea, and as the 40–60, 50–50, and 70–30 inorganic-organic ratios. By the fourth period the sulfate of ammonia, the tankage, and the 60–40 ratio had leached to the same extent. The cylinder receiving fish, however, did not lose nitrogen to this extent until the fifth period, or after 70 days had elapsed and the equivalent of a total of 7½ inches of rainfall had been added.

The treatments ranked as follows with respect to the total amount of nitrate leached: 1. nitrate of soda; 2. the 80–20 ratio; 3. ½ nitrate of soda—½ sulfate of ammonia; 4. the 70–30 ratio; 5. the 50–50 ratio; 6. the 40–60 ratio; 7. urea; 8. the 60–40 ratio; 9. sulfate of ammonia; 10. fish; 11. tankage. These may also be considered the relative rates of availability.

Cylinder 9, which received its nitrogen from the 60–40 ratio is evidently out of line, although no satisfactory explanation has been found. It may be due in part to a greater evaporation from the surface of the soil and hence to a slightly smaller total volume of leachings, as shown in table 8. For the first three periods, however, the volume of leachings from this cylinder was greater than from some of the others. The growth of oats, planted in these cylinders after the 112-day period, seems to indicate that an appreciable amount of the fertilizer nitrogen added to this cylinder remains in the soil. In fact, for all the cylinders the growth of this crop is inversely proportional to the amount of nitrate leached.

At the start of this experiment no analyses were made to determine the amounts of ammonia-nitrogen which may have leached from the cylinders receiving sulfate of ammonia. It is not probable that any appreciable amount of ammonia-nitrogen was leached as such. The following considerations would support this belief: (*a*) the fact that the soil was slightly acid, pH 6.4; (*b*) the fertilizer was added to the surface 3 inches only; (*c*) 14 days elapsed between the moistening of the soil and the date of the first leaching; (*d*) the actual amount and the proportion of *nitrate* leached at the first period from the cylinder receiving nitrate of soda were relatively small. The fact that nitrates leach much more rapidly than ammonia, especially in acid soils, has long been recognized. Fraps (28) has shown that 500-gm. portions of soil, to which ammonium chloride had been added to the extent of 51.7 p.p.m. of ammonia nitrogen, when leached immediately, retained from 61 to 98.5 per cent of the ammonia added. For cylinder 2, to which all of the nitrogen added was in the form of sulfate of ammonia, the 316.6 mgm. of nitrogen added to 5500 gm. of soil is equivalent to 57.5 p.p.m. of ammonia nitrogen. In view of the aforestated considerations and conditions of this experiment, it is improbable that any appreciable amount of nitrogen was lost in the leachings in the ammonia form.

Considering from another angle, this question for cylinder 2, the 5.5 gm. of fertilizer added contained 1.493 gm. sulfate of ammonia. Adding the approximate 1200 cc. of capillary moisture held by the soil in each cylinder, to the 825 cc. of water used to leach the soil, gives a total of approximately 2 liters of water present at each leaching. These amounts of water and sulfate of ammonia would give approximately a $\frac{1}{14}$ N solution. Wolkoff (82) found that on adding 4 cc. of a $\frac{1}{32}$ N ammonium sulfate solution to 20 gm. of Sassafras medium sandy loam, the freezing point depression was lowered 47 per cent because of absorption. Garretson (32) in studying the soils of Java, added sulfate of ammonia in amounts equal to 1 per cent of the weight of the soil. He found that after nitrification, about 81.5 per cent of the added nitrogen could be leached as nitrate; whereas before nitrification, from one to two per cent only of the added nitrogen was leached by the same procedure. From the foregoing it seems permissible to assume that the leaching of nitrogen in the form of ammonia did not appreciably influence the total loss of nitrogen in the drainage water.

The rapid leaching of nitrates during the early periods from cylinder 4, in which urea was used entirely as the source of nitrogen, is in complete agreement with the pot experiments of Series I and II. The relatively small total amount of nitrate leached from this cylinder during the entire period, is also in agreement with the data of the preceding experiments, in that the total nitrate accumulation from this material was in many instances less than from sulfate of ammonia, fish, or tankage.

There are several factors which influence the leaching of nitrogen applied to soils in commercial fertilizers. Briefly, they are: the chemical form in which the nitrogen is applied, the organic matter and nitrogen content of the soil, the microbiological flora, the mechanical composition, the moisture content, and the soil temperature, all of which influence the rate of nitrate formation. The influence of these factors was demonstrated in the pot cultures of Series I and II. In this Series the influence of various combinations of nitrogenous materials on the rate of nitrification is apparent. Since all useful nitrogenous fertilizer materials produce appreciable amounts of nitrate nitrogen in the soil within the growing season in which the application is made, the question resolves itself to that of a balance between the *rate* of nitrification and the soil and climatic factors which favor or inhibit rapid leaching. The combinations of nitrogenous materials employed in this experiment indicate that within certain limits the rate of nitrate formation may be controlled by the judicious mixing of various materials.

It is well known that, because of climatic and soil temperature conditions, early vegetable crops can best be produced on sandy soils. Such soils are always relatively deficient in clay and silt, i.e. in colloids and the materials from which colloids may readily be formed. Although the soil selected for these leaching experiments may present a rather extreme type of these soils, in that it contains nearly 89 per cent total sands and only 11 per cent silt and

clay, it affords an excellent medium for the comparison of nitrogenous materials. Furthermore, considerable areas of this soil exist, and may be cropped successfully when the sources of nitrogen are adequatey balanced, and the method and time of application are adapted to the existing conditions.

There is a definite and well defined nitrogen problem with these soils. Their mechanical composition, the summer drouth, and the cropping system to which they are best adapted, all make it impractical to attempt to build up high organic matter and total nitrogen contents. The cash crops require appreciable quantities of nitrate nitrogen early in the season, in order to force growth against the influence of unfavorable soil and air temperatures. At such times the soil temperature is usually too low to promote rapid nitrification of many of the commercial organic materials used in fertilizers. Consequently some nitrate nitrogen must be included. Small local areas in the Sassafras soils and extensive areas of the Norfolk soils, have subsoils containing even less silt and clay than the surface soil. The present experiment has shown that soils deficient in colloidal material have a relatively small capacity for the absorption of nitrates.

At the experimental field at Snow Hill, Maryland, there was a total rainfall of 18.2 inches during the growing season for the early potato crop, from March 26 to June 30, 1924. In addition, the date of planting had been considerably delayed by excessive rainfall prior to March 26. Both on May 24 and June 9, more than 3 inches of rain was measured by the rain-gauge within 24-hour periods. On May 18 nearly 2 inches of rain fell, and on March 29, April 6, and May 21, 1 inch or more of rainfall was recorded. These heavy precipitations undoubtedly leach a considerable proportion of the nitrate nitrogen present at the time from the surface soil to the subsoil. Unless the subsoil has an appreciably higher silt and clay content than the surface soil and if its capillary contact is broken by a layer of relatively coarse sand, it is doubtful whether much of the nitrate-nitrogen leached is again brought to the surface. Especially in these tidewater regions, lying from 5 to 20 feet above mean sea level, and in which the pemanent water table is found at a depth of 2 to 4 feet, the recovery of nitrates once leached from the surface soil is evidently quite small.

The duration of the leaching experiments was 112 days, during which time the equivalent of 12 inches of rainfall had been added to each cylinder. In the field during the 1924 season, this amount of precipitation had occurred within 62 days after the early potato crop had been planted. Table 7 shows that, from cylinders 1, 6, and 11, which received 100, 50, and 40 per cent respectively of the added nitrogen as nitrate of soda, the equivalent of 92 to 85 per cent of the fertilizer nitrogen had been leached. In fact 6 inches, or one-half the amount of rainfall, in 6 days less time, leached 91.6, 82.4, and 84.0 per cent respectively of the amount of nitrogen added to these cylinders. From this it is evident that for these soils when the amount of nitrate present is in excess of the feeding-power of the crop plus the absorptive capacity of the soil, the

amount of nitrate leached depends entirely on the characteristics of the subsoil and the distribution and amount of rainfall. The malnutrition of the early potato crop, so frequently observed on these soils, may thus be explained by the fact that too great a portion of the fertilizer nitrogen was supplied as nitrates or readily nitrifiable materials.

Aside from the growing of leguminous green manure crops whenever practicable, the nitrogen problem for these soils resolves itself into that of using a fertilizer that will yield sufficient nitrate nitrogen to produce the early growth desired, but which at no time will give a large accumulation of nitrate to be lost in the drainage water. To obtain this result all of the type materials compared in these experiments can be employed profitably, but the first essential is a clear understanding of the soil conditions influencing the rate at which each material produces nitrate nitrogen.

SUMMARY AND CONCLUSIONS

1. The optimum soil-moisture content for nitrate production from various nitrogenous materials applied in a 7–6–5 complete fertilizer, was found between 50 and 60 per cent of the water-holding capacity for Norfolk sandy loam soil.

2. There was a larger nitrate accumulation from urea at 70 per cent of the water-holding capacity of the soil than from sulfate of ammonia, dried ground fish, or packing house tankage.

3. After the first period of rapid nitrification, the fluctuations of nitrate nitrogen in this soil appear to be the result of the activity of soil microörganisms, rather than of differences in soil-moisture, temperature, or reaction.

4. Up to 20 to 30°C., which was the highest temperature range employed, nitrate *production* from sulfate of ammonia, urea, dried ground fish, packing-house tankage, and activated sewage-sludge increased directly with the temperature.

5. At all temperatures, urea showed the most rapid rate of nitrification; at all except the lowest temperature level, sulfate of ammonia gave the highest ultimate accumulation of nitrate.

6. When both rate of nitrate *production* and rate of nitrate *accumulation* in this soil are considered, the materials employed rank in the following order: nitrate of soda, urea, sulfate of ammonia, dried ground fish, packing-house tankage, and activated sewage sludge.

7. The leaching of nitrates from Norfolk sandy loam soil, following an application of a 7–6–5 fertilizer equivalent to 2000 pounds per acre, varied directly with the proportion of the nitrogen supplied by nitrate of soda in the mixture.

8. When used as the sole source of nitrogen in this analysis ratio, there was little difference in the total amounts of nitrates leached from sulfate of ammonia, urea, dried ground fish or packing-house tankage; although more nitrate-nitrogen leached during the early periods from the cylinder receiving nitrogen from urea.

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